STUDY OF A PROCESS BASED ON SALT-FREE DYEING OF CELLULOSIC FIBRES

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ABSTRACT

Textile processing industries need effective solutions to address the problems posed by the use of salt in the dyeing process that has led to the accumulation of salt slurry in the industrial sector. As a result, an alternative for salt use is imminent and oxidation and hyperbranched polymer grafting of cotton is an effective solution to the above-mentioned problem. The methodology used in this study consists of the optimal condition of sodium periodate oxidation, hyperbranched polymer grafting of cotton fibre (HGCF) with Lupasol® P and the red reactive dyeing process.

The optimal condition of oxidized cotton fibre is found to be oxidized cotton fibre in 2 g/L sodium periodate solution at a temperature of 40 °C for 60 minutes. After grafting the oxidized cotton fibre with Lupasol® P, the dyeing process is carried out using red reactive dyes with five different conditions involving a different concentration of salt. It is found that the treated cotton fibre with a concentration of 50 % salt concentration has the highest K/S value compared to untreated cotton fibre with a concentration of 100 % and 50 % salt concentration. The K/S value of the treated cotton fibre with no salt concentration is similar to that of the untreated cotton fibre with a concentration of 100 % salt. The washing fastness and rubbing fastness also resulted in a good grade of standard grey scale readings.

Referring to all the results of this study, it is shown that the use of salt in the dyeing process can be minimized by pre-treatment of cotton fibre. If further studies are carried out, such as studying the reduction of the concentration of salt in the dyeing process of the treated cotton fibre to achieve the same results as the untreated cotton fibre with 100 % salt concentration, it may help to gather more information in order to achieve the goal of a salt-free dyeing process.

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AC	average aldehyde content
AGU	anhydroglucose
CCT	correlated colour temperature
CIE	Commission Internationale de l'Eclairage
CIELAB	CIE L* a* b*
DAC	dialdehyde cellulose
DP	degree of polymerization
Fmax	average maximum force
g/cm^3	gram per cubic meter
g/L	gram per litre
HGCF	hyperbranched polymer grafted cotton fibre
K	Kelvin
K/S	colour strength
M	molarity
mPa.s	miliPascal-seconds
MW	molecular weight
PEI	polyethyleneimines
SED	spectral energy distribution
μm	micrometre

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1 INTRODUCTION

1.1 BACKGROUND

Cotton fibres are commonly used in the textile industry because of their outstanding hygroscopic characteristics, air permeability, biodegradability, no static electricity, and this fibre is well known for its comfort, good absorption of moisture and good wicking properties etc.[1]

The reactive dyes are the most popular for dyeing cotton because of their colour brightness, broad colour gamut, and all-round excellent colour fastness properties of the resulting dyeing.[2] Cotton is negatively charged in aqueous medium hence it will repel anion dye during dyeing. Due to its repulsion, a large amount of salts is used to offset the repulsion in a dye bath. Because cotton has only moderate affinity for most reactive dyes, big amounts of electrolytes such as sodium chloride, NaCl or sodium sulphate, Na_2SO_4 are usually needed for exhaustion. Therefore, for some dyes, dye bath exhaustion and fixation can still be as small as 50 %.[1]

High concentration of salt and poor use of reactive dye fixation can contribute to environmental issues such as highly coloured effluent with high salt content. A tiny part of electrolytes is discarded during effluent treatment, the residual result in increased river salinity, marine life disturbance, freshwater scarcity, groundwater infertility, and elevated values of BOD / COD (Biological Oxygen Demand / Chemical Oxygen Demand).

To solve this issue, this study aims to discover a path by grafting hyperbranched polymers onto cellulose to eliminate the use of salt in this type of process. The best way to solve the absence of affinity for cotton to reactive dyes in making salt-free reactive dyeing is to modify the cotton fibre to boost dye-fibre interaction.

A specific chemical modification of cellulose using sodium periodate oxidation is the first methodology taken in this study. Because of the three hydroxyl groups accessible for oxidation within one anhydroglucose unit and the polymeric character of the cellulose, a wide range of structural modification is feasible. The next method is a fibre modification technique based on hyperbranched polymer that is retreated with oxidized cotton fibre because it believes that pre-treated cellulosic fibre with polymer provides a chance to increase both the substantivity and reactivity towards reactive dyes under neutral conditions using the cotton cationization concept.[1] The reactive dyes that are anionic (negative charged) in solution are attracted to the fibre's positive charge, forming a cross-link within the fibres that eliminates the salt demands for adequate dye exhaustion.

1.2 OBJECTIVES

- To produce maximum aldehyde compound by using sodium periodate oxidation as intermediate for the dyeing process.
- To introduce maximum amino groups in cellulose fibre using hyperbranched polymer for the process of cationization of cotton.
- To reduce the usage of salts in the dyeing of cotton.
- To achieve maximum dye fixation.
- To reduce environmental pollution.

2 LITERATURE REVIEW

2.1 COTTON CELLULOSE

Cellulose is a renewable, biodegradable and cheap raw material with appealing characteristics as a biomaterial. It becomes a high-strength and durable wood material in conjunction with lignin and hemicellulose. Cellulose has been used as a building material in the form of wood and clothing for thousands of years, as well as an energy source.[3]

Cotton is the purest natural form of cellulose. Cotton fibres are one of the most important types of fibres in the world even though there are a growing amount of synthetic fibre types available and a high quantity of wood cellulose in the market. Because of its excellent characteristics including regeneration, biodegradation, softness, skin affinity, hygroscopic properties, strength and dyeability, cotton is widely used in clothing fields.[4]

Cotton fibres have a structure of fibrillar as seen in Figure 1. The entire cotton fibre contains 88 to 96.5 % of cellulose, while the rest are non-cellulosic polysaccharides, up to 10 % of the total fibre weight. Non-cellulosic components are made up of pectin, fats and waxes, proteins and natural colourants. The main wall is only 0.5 - 1 μm dense in mature fibres and includes about 50 % cellulose. The secondary wall, which contains approximately 92 - 95 % cellulose, consists of concentrated layers with alternative shaped twists.

The layers are densely packed elementary fibrils, arranged in micro fibrils and macro fibrils. Strong hydrogen bonds hold them together. The lumen is the fibre centre. Cotton is made up of polysaccharide cellulose almost completely. Cotton cellulose consists of crystalline fibrils that vary in complexity and length and are linked by less structured amorphous areas with an average proportion of approximately two-thirds of crystalline and one-third of non-crystalline material based on the determination technique.

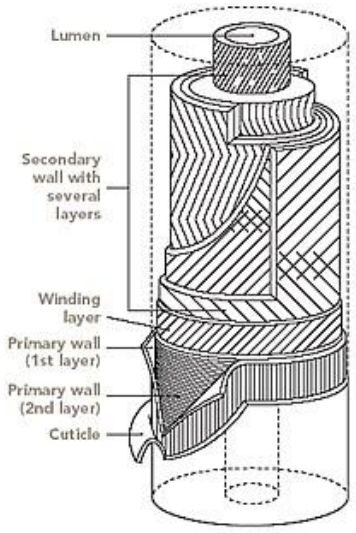


Figure 1 A schematic representation of cotton fibre showing its various layer [5]

Cellulose's chemical structure is simple, composed of anhydroglucose units (AGU) joined to form linear polymeric chains by β-1,4-glucosidic bonds, see Figure 2. A cotton cellulose molecule's chain length, or degree of polymerization (DP), represents the number of anhydroglucose units connected to form the chain molecule. Cotton DP may be as big as 14 000, but various purification procedures with alkali can readily reduce it to 1000–2000. Probably the crystalline regions have a DP of between 200 and 300. Accordingly, cotton's molecular weight (MW) generally ranges from 50,000 to 1,500,000 depending on the cellulose source.[5]

Through hydrogen bonding and Van der Waals forces, the individual chains conform to each other along their lengths. The cotton fibre's physical characteristics as a textile material, as well as its chemical behaviour and reactivity, are determined by cellulose molecules' arrangements with regard to each other and the fibre axis.[5]

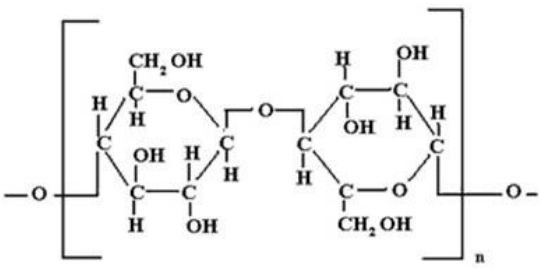


Figure 2 Chemical structure of cellulose [5]

Cellulose is a polar molecule and the native structure is hygroscopic, which means that big amounts of water can be absorbed, leading to swelling. However, given its hydrophilic and polar features, cellulose does not dissolve in water and can be transformed into a hydrophobic or even a superhydrophobic material by modification. Furthermore, the strong bonds stop melting of cellulose. Because of the hydrogen bonding mechanism and the tightly packed structure, cellulose becomes extremely crystalline. There is cellulose in distinct degrees of crystallinity, clearly there are also amorphous areas as no polymeric substance can be completely crystalline.

Each AGU includes three hydroxyls groups that are fully or partially available for reagents for derivation. Two secondary hydroxyl groups connected to two secondary carbons, C2 and C3, and one primary hydroxyl group connected to a primary carbon, C6 as seen in Figure 3. By physical adsorption or by covalent binding of polymers or tiny molecules, specific functional groups can be introduced. Normally, owing to less steric hindrance, a reaction happens easier at the primary carbon or hydroxyl group location. However, based on the chemistry employed, all three hydroxyl groups can be altered and it is usually hard to quantify which OH-group has been altered.[4]

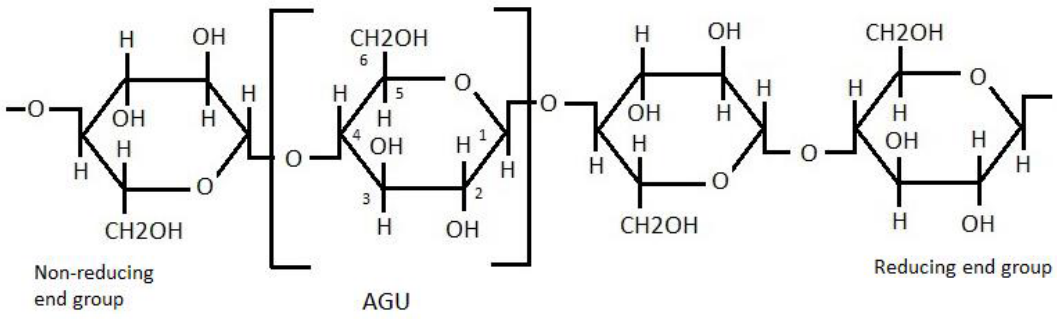


Figure 3 Schematic representation of a cellulose chain with the repeating unit AGU [4]

2.2 SODIUM PERIODATE OXIDATION

In cellulose chemistry, chemical modification of cellulose using oxidizing agents is quite frequent. Depending on the nature of the oxidant and the conditions of oxidation, aldehyde, ketone and carboxyl groups may be created in the cellulose during oxidation. Most oxidations proceed with rather low selectivity and oxidation of cellulose with sodium periodate, $NaIO_4$ is a highly selective reaction.[6] Since sodium periodate is relatively expensive and can be harmful to the environment, therefore, its recyclability is also of great significance.

Employing sodium periodate as an oxidizing agent can produce the cellulose derivate dialdehyde cellulose (DAC). Periodate oxidation can result in decreased crystallinity where the fibres are more flexible and thinner. With the aid of heating, a complete periodate-oxidized is soluble in water while partially oxidized cellulose is not soluble in water. Sodium periodate is periodic acid's inorganic salt and consists of sodium, iodine and oxygen. Sodium periodate may occur as IO_4^- or IO_6^{5-} in two forms and IO_3^- is also produced as a by-product. It is the metaperiodate form, IO_4^-, with fewer oxygen molecules that reacts with an AGU when DAC is produced according to:

$$Cellulose + NaIO_4 \rightarrow Dialdehyde\ cellulose + NaIO_4 + H_2O \quad (1)$$

The conversion of dihydroxyl groups by sodium periodate oxidation to dialdehyde cellulose (DAC) is a significant process commonly used in cellulose derivation to facilitate the polymer in further reactions. Sodium periodate oxidation transforms 2, 3-dihydroxyl groups into two groups of aldehydes without major side reactions via a cyclic iodate diester as seen in Figure 4. This reaction selectively cleaves the C2-C3 bond of the glucopyranoside ring when introduced to glucose in the cellulose chains according to the Malaprade reaction mechanism.[7]

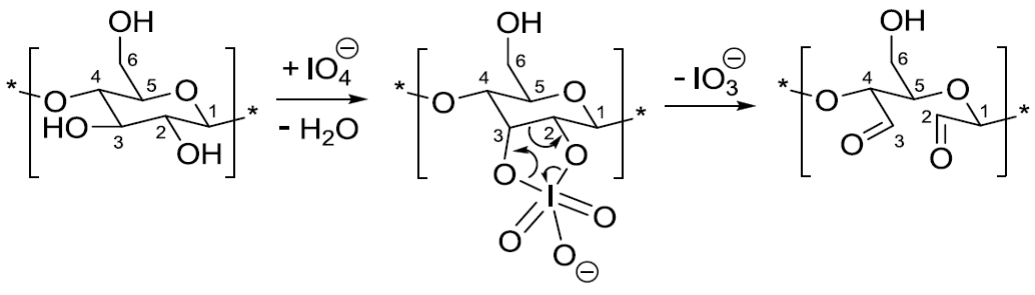


Figure 4 The schematic formation of DAC through the periodate oxidation of cellulose [4]

DAC is biodegradable and biocompatible which can be a great potential to be used in several applications and serve as an intermediate for other cellulose derivatives. The possible modification reactions that DAC can undergo involves the use of bisulphite to produce sulfonates, and if amines are added, imines are produced. This reaction is strongly affected by factors such as time and temperature, and the reaction is delayed at room temperature. However, the temperature should not be too high as the sodium periodate is unstable and there is a risk of iodine decomposition and liberation from iodate by-product (IO_3^-) especially after some time above 55 °C.[4]

The degree of oxidation is the amount of C2-C3 bonds that are transformed into dialdehydes. The degree of oxidation can be controlled by the quantity of sodium periodate introduced in conjunction with the reaction conditions. Various methods have been used to determine the degree of oxidation. The most commonly used mechanism includes reaction with hydroxylamine hydrochloride, $2NH_2OH{\cdot}HCl$, accompanied by titration with sodium hydroxide. This is an oxime reaction in which hydroxylamine hydrochloride reacts with all available aldehyde groups, see Figure 5. Hydroxylamine hydrochloride is a hazardous chemical accused of creating cancer and is therefore unlikely to operate with. [4]

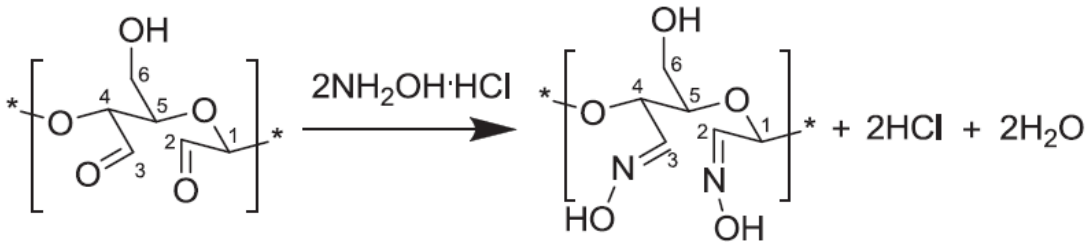


Figure 5 The reaction pathway between dialdehyde cellulose and hydroxylamine hydrochloride [4]

To study the mechanical properties of cellulose following the alteration of oxidation, the tensile strength of the fibre is evaluated to determine the stress and strain of the fibre. The formation of soluble fragments as a consequence of cellulose decomposition during sodium periodate oxidation was determined by measuring the yield loss using the direct gravimetric method. All tests conducted out can determine the optimum condition of the cotton fibre after sodium periodate oxidation.

2.3 HYPERBRANCHED POLYMER GRAFTED COTTON FIBRE (HGCF)

Periodate oxidation of cotton fibre results in a ring-opening product comprising two aldehyde groups created by the oxidative scission of the AGU units C-2 and C-3 in the fibre molecule. Most researchers concentrate on the introduction of cationic groups such as amino or ammonium groups into cotton fibres for interactions with anionic dyes. The next preparation of the study is to prepare an amino-terminated hyperbranched polymer grafted cotton fibre (HGCF) by reacting the aldehyde groups of the oxidized cotton fibre with the amino groups of the Lupasol® P as shown in Figure 6. The HGCF fabrics produced under optimal conditions showed significantly increased colour strength when dyed with reactive dye using salt-free dyeing.[8]

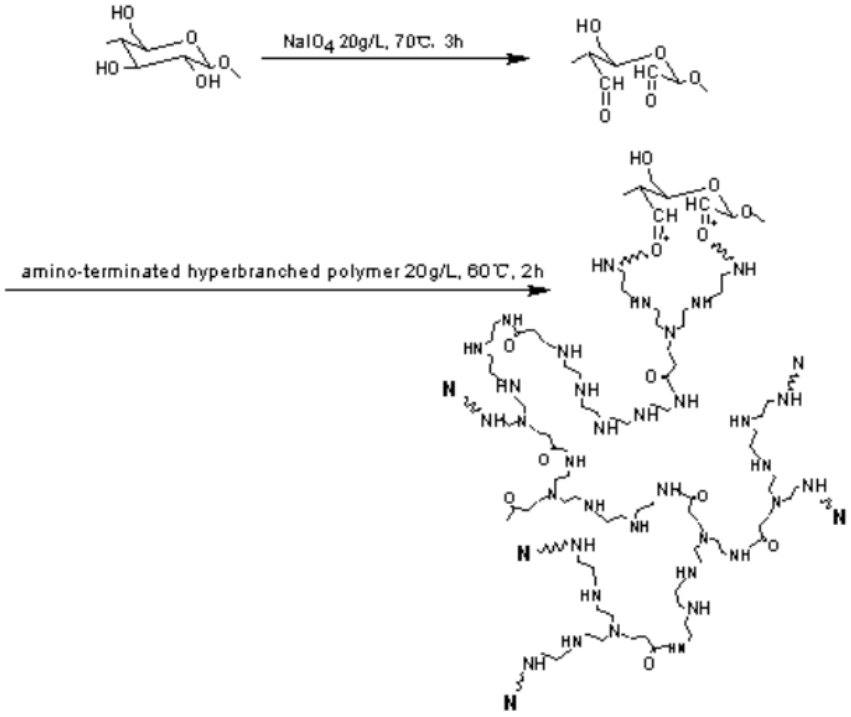


Figure 6 Preparation of HGCF [9]

Lupasol® is made up of various polymer types with distinct structures. Lupasol® products are multifunctional cationic polyethyleneimines (PEI) with a branched polymer structure as shown in Figure 7. Their composition is demonstrated by the following general molecular formula:

$$-(CH_2 - CH_2 - NH)_n - \qquad (10 < n < 105) \qquad (2)$$

The proportion of nitrogen to carbon in polyethyleneimines is 1:2 so all known commercial polyamines have the biggest possible amino group density. Polyethyleneimines have a definite ration of primary, secondary and tertiary amino groups.[10]

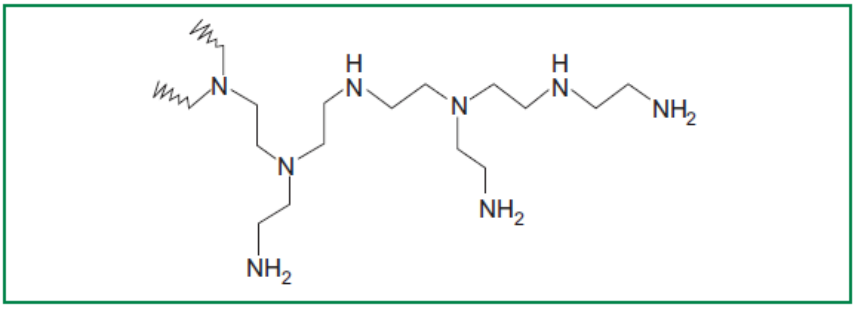


Figure 7 Polyethyleneimines (PEI) with a branched polymer structure [10]

Lupasol® P is used in this study as a hyperbranched polymer. It is a multi-functional cationic PEI with a branched polymer structure. Lupasols' distinctive properties enable them to improve and alter surface characteristics after surface modification and protect materials. Lupasol® P is a colourless to pale yellow, aqueous solution with a honey-like texture and a 50 % aqueous formulation of PEI with a molecular weight of around 750,000.[11] According to BASF; the chemical company, Lupasol® P is improving reactive dye fixation on cotton. It may be used during pre-treatment or post-treatment.[10] Lupasol® P is in all proportions miscible with water and cannot identify importunity of ethylenimine. It has three types of bonding: ionic, hydrogen and van der Waals.[12] Table 1 below consists of specifications and typical physical properties of Lupasol® P.

Table 1 Specifications and typical physical properties of Lupasol® P [11]

SPECIFICATIONS	
Solid content	48.0 – 52.0 %
Viscosity @ 20 °C	25 000 mPa.s
TYPICAL PHYSICAL PROPERTIES	
Density (20 °C)	1.09 g / cm^3
Pour Point	-3 °C
Ph	10-12
Concentration	50 %
Average Molecular Weight	750 000
Common Chemical Name	Polyethyleneimines (PEI)
CAS Number	9002-98-6

For more than 50 years, Lupasol® P has been used in the paper industry to increase paper strength and flocculate fines for recycling in disposal rivers. This is its biggest use today. Lupasol® P also encourages metal surfaces adhesion and increases inhibitors of corrosion. Moreover, Lupasol® P hosts active enzymes for use in industrial chemical synthesis in porous and non-porous supports and immobilized PEI efficiently filters blood plasma endotoxins and pathogens. Lupasol® P can be placed in closed containers for approximately one year. Freezing can occur at temperatures below 0 °C, but it is fit for use after thawing and stirring.[11]

2.4 DYEING OF COTTON FIBRE

At the end of this study, the HGCF will be dyed with reactive dyes. Reactive dyes are the only type of dye with a reactive group that chemically associates with fibre polymer molecules and forms a covalent bond. This covalent bond is created between the reactive group and the cellulosic fibre polymer terminal -NH2 (Amino) group. This covalent bond's strength is more than ionic bond, hydrogen bond, and the force of attraction of Vander Waal. This makes the reactive group an essential component of the fibre.[13] Reactive dye could not be removed under normal conditions through frequent treatment with boiling water. Consequently, the dye becomes part of the fibre, resulting in exceptional colour fastness for washing.[14]

A common reactive dye's characteristic structure involves the chromogen that contributes to the colour display, reactive groups that enable chemical reactions between fibre and dye, the bridging link that links the reactive group with chromogen and solubilizing group that enhances the dye's solubility. As the name implies, the reactive dye has reactive groups to chemically form covalent bonds and become part of with cotton, rather than as an independent coloured substance within the fibre. Figure 8 shows the addition reactions between dye and cellulose and Figure 9 shows the substitution reactions between dye and cellulose.[14]

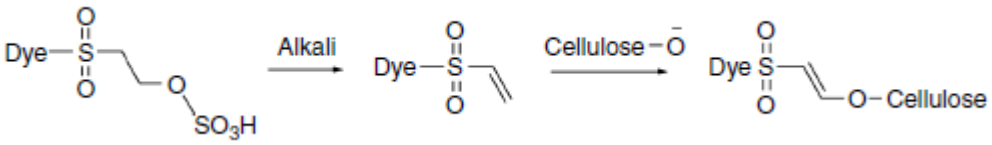


Figure 8 Addition reaction between cellulose and reactive dye

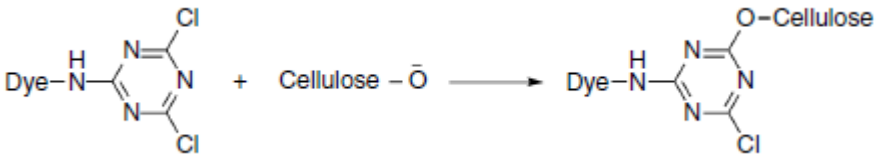
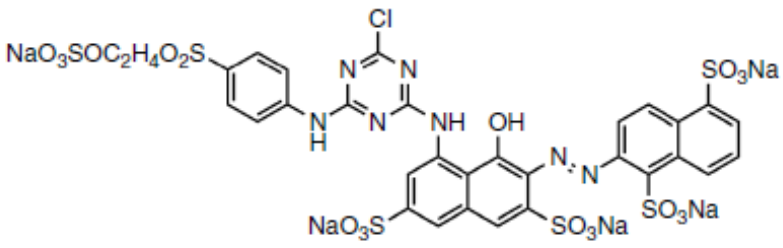
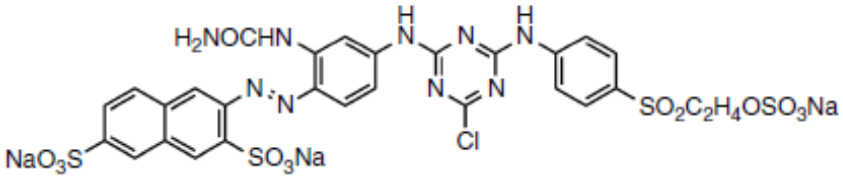


Figure 9 Substitution reaction between cellulose and reactive dye [14]

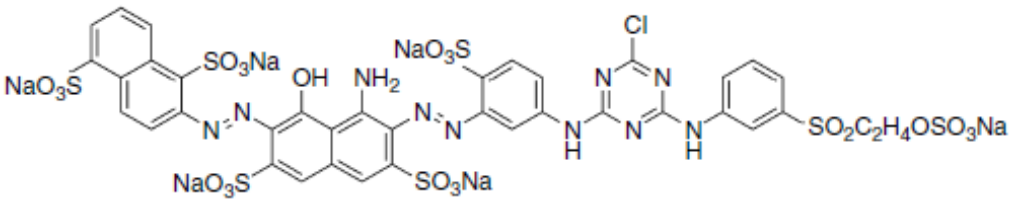
Dye selection, given both the dyeing behaviour and the price of production, is the first significant problem in dyeing. Colour that matches three dyes nowadays, such as three primary colours in red, yellow, and black, is very common in practice. The compatibility of the chosen three dyes should, therefore, be excellent, i.e. the dyes should have comparable dyeing behaviour, including tone-on-tone build-up characteristics, equivalent robustness to distinct dyeing circumstances, and no blocking effect between them. Figure 10 shows a set of typical three primary colour commodity dyes applied to match medium and deep shade in red, yellow, and blue. There are also ranges of three primary colour commodity dyes employed for corresponding light shade with greater colour fastness.[14]



C.I. Reactive Red 239



C.I. Reactive Yellow 176



C.I. Reactive Blue 222

Figure 10 A set of typical three primary colour commodity dyes applied to match medium and deep shade in red, yellow, and blue.[14]

2.5 COLOURIMETRY

Colourimetry is the science element that deals with colour measurement. A physical sample is needed for a colour to be completely determined, although the device design may also be used. Objective instrumental evaluation will enable us to identify a colour. Colourimetry is based on the research of the physical magnitudes that distinguish colour and the applications that enable it to be duplicated as an imitation of human colour vision utilizing devices.

Colour is the consequence of colourants physically modifying light as identified by the human eye called a response process and expressed in the brain as a perceptual process that induces psychology. To see the light, the existence of colour requires a light source, an object, and an observer. An opaque object's reflection of rays as a function of wavelength defines the object's colour. A textile material's colour is often one of its most important characteristics.[15]

A surface's reflectance distribution is constant and independent of the illumination under which it is regarded. Under various illuminations, however, the surface colour changes. When we talk about illuminants, their spectral distribution of radiant flux which is spectral power distribution in Figure 11 is usually concerned. There are many distinct forms of light under which the images can be viewed, the most significant being daylight. Distinguishing between the origin and the illuminant is essential. Whereas a source relates to a physical emitter of radiant energy, such as a lamp or the sun and sky, an illuminant relates to an incident involving a specific distribution of spectral power on the observer's subject.[15]

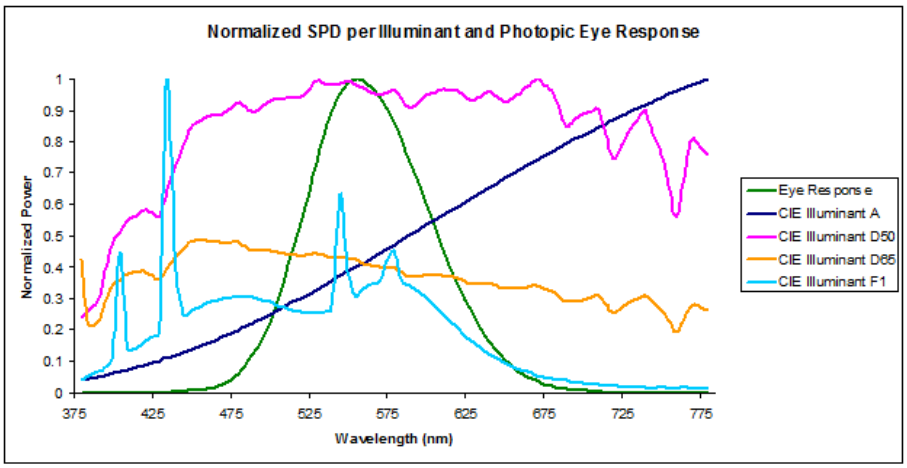


Figure 11 Spectral Power Distribution [16]

The CIE (Commission Internationale de l'Eclairage) advised the use of various illuminants derived from the spectral energies of various light sources over the years. CIE illuminant D65, with an approximate correlated colour temperature (CCT) of 6500 K (Kelvin), contains a spectral energy distribution (SED) which is a good approximation of daylight average. D65 is the primary illuminant for applications for colour measurement. CIE illuminant A, with an approximate correlated colour temperature of 2856 K, was designed to define the typical light from a tungsten filament lamp filled with gas. At the longer wavelengths, the amount of energy emitted is far greater than that emitted at the shorter wavelengths. CIE illuminant F1 which is fluorescent illuminant, with an approximate correlated colour temperature of 4000 K, is known commercially as TL84 and contains a spectral distribution of energy that is a good approximation of store light. Fluorescent illuminants at narrow bandwidths have very high SEDs.[15]

Tristimulus values are a colour's fingerprints and are calculated by taking into consideration the basic colour concepts that are the object, illumination, and observer. They represent the quantities of standard lights to reproduce a colour that are red, green and blue. The CIE order system is numerical. In 1976, CIE recommended colour space for CIE L* a* b* which also known as the CIELAB system and colour differentiation formula. Spectrophotometers are the most popular and widely recognized tools, providing colour data in the L*a*b* colour space. CIELAB colour space was developed through experiments that correlate tristimulus values with visual colour perceptions from attempts to transform the X, Y, Z system which is tristimulus value into a visually uniform colour system.[15]

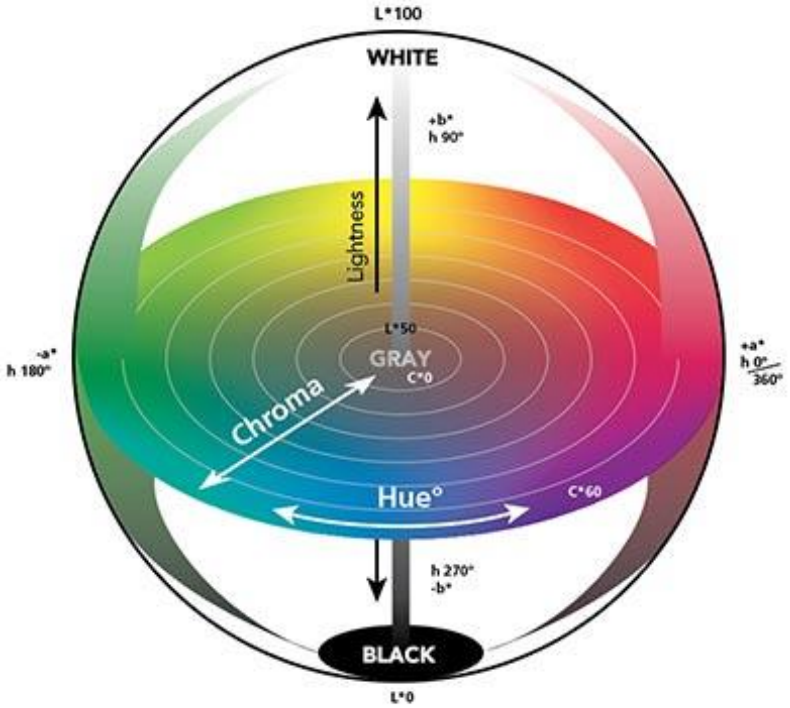


Figure 12 CIELAB Colour Space [17]

The coordinates of L*, a* and b* are the numerical outcomes by established formulations and represent the location of a colour shade in the colour space of CIELAB. CIELAB colour space is an opponent-type colour space with three axes perpendicular to each other. The a* axis represents the opponent's red-green pair (a*+ is red and a*- is green), the b* axis represents the opponent's yellow-blue pair (b*+ is yellow and b*- is blue), and the white-black opponent pair represents the L* axis. The coordinates a* and b* define a plane of chromaticity. The third axis, L *, is the axis of lightness, perpendicular to the plane of chromaticity, ranging from 0 to 100 for white. Colours are mapped on the panel a* - b* (L* = 50; a* = 0, b* = 0) and the angle of chroma and hue is calculated on this panel using results a* and b*.[15] CIELAB colour coordinates are calculated as follows:

$$L^* = 116\left(Y / Y_n\right)^{1/3} - 16 \tag{3}$$

$$a^* = 500\{(X / X_n)^{1/3} - (Y / Y_n)^{1/3}\} \tag{4}$$

$$b^* = 200\{(Y / Y_n)^{1/3} - (Z / Z_n)^{1/3}\} \tag{5}$$

$$C^*_{ab} = \sqrt{(a^*)^2 + (b^*)^2} \tag{6}$$

$$h = \tan^{-1}\left(\frac{b^*}{a^*}\right) \tag{7}$$

Whereas L* is Lightness axis, a* is Red-Green axis, b* is Yellow-Blue axis, C* is Chroma, h is hue angle, X, Y and Z are tristimulus values of the illuminant and X_n, Y_n and Z_n are tristimulus values of the colour. CIELAB (1976) colour difference is calculated as follows:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{8}$$

In the calculation of the Δ values, the calculation is made according to “sample value-standard value”.

3 RESEARCH METHODOLOGY

3.1 MATERIALS

All materials used in this study were of analytical grade and were provided by the laboratory. The sample for each cotton fabric shall be labelled according to the name of the sample, which shall contain three samples for each condition, reaction time, temperature and sodium periodate concentration used consecutively. For example, A.10.30.1 is sample A with conditions consisting of a reaction time of 10 minutes, a temperature of 30 °C and a sodium periodate concentration of 1 g/L.

Cotton fabric is washed before using it in an experiment with a surfactant (Hospatal DTC) that will also be used to clean the dyed fabric. The main chemicals used in this study are sodium periodate, $NaIO_4$ for oxidation, Lupasol® P (Polyethyleneimins) as an amino-terminated hyperbranched polymer and red reactive dye (Red Cibacron ZGE). The auxiliary chemicals used in this study are sodium carbonate, Na_2CO_3, sodium hydroxide, NaOH, sodium sulphate, $NaSO_4$ and hydroxylamine hydrochloride, $NH_2OH.HCl$. Deionized water has been used throughout the experiment. Figure 13 shows some of the chemicals used in the laboratory.

Figure 13 Chemicals used in laboratory

3.2 SODIUM PERIODATE OXIDATION OF COTTON FIBRE

Cotton fibre is cut in 20 cm x 5 cm and washed at 40 °C using a 20 g surfactant of Hospatal DTC. Then, the cotton fibre is dried in the oven at 60 °C until the weight is constant and the weight is noted. Cotton fibre needs to be completely dried and hence several measurements of weight have to be taken into account to obtain the average weight. The sodium periodate solution is prepared with a different concentration of 1 M, 2 M and 4 M. Cotton fibre is then immersed in an aqueous sodium periodate solution with a different concentration (g/L) at a liquor ratio of 1:30 (1 g cotton fibre / 30 mL) in a steel container to prevent the photo-induced decomposition of sodium periodate. Volumetric flask used to store sodium periodate must be covered with aluminium foil to prevent sunlight from entering the volumetric flask as shown in Figure 14.

Figure 14 Steel containers and volumetric flasks covered with aluminium foil

Finally, the solution is stirred with the Original Hanau Linitest machine in Figure 15 at 40 rpm in the water bath at the desired reaction temperature (°C) for different reaction times (min) in the absence of light as shown in Table 2. Each sample will have different conditions for three different concentrations, temperatures and reaction times, totalling up to 27 samples. Each sample shall be repeated three times and shall be named samples A, B and C, therefore the total samples shall be 81 pieces and all data shall be shown in Annex 1.

Figure 15 Original Hanau Linitest Machine

Table 2 Conditions of sodium periodate oxidation

Concentration of periodate, (g/L)	Temperature, T (°C)	Reaction time, t (min)	R/B
1	30	10	1:30
2	40	30	1:30
4	50	60	1:30

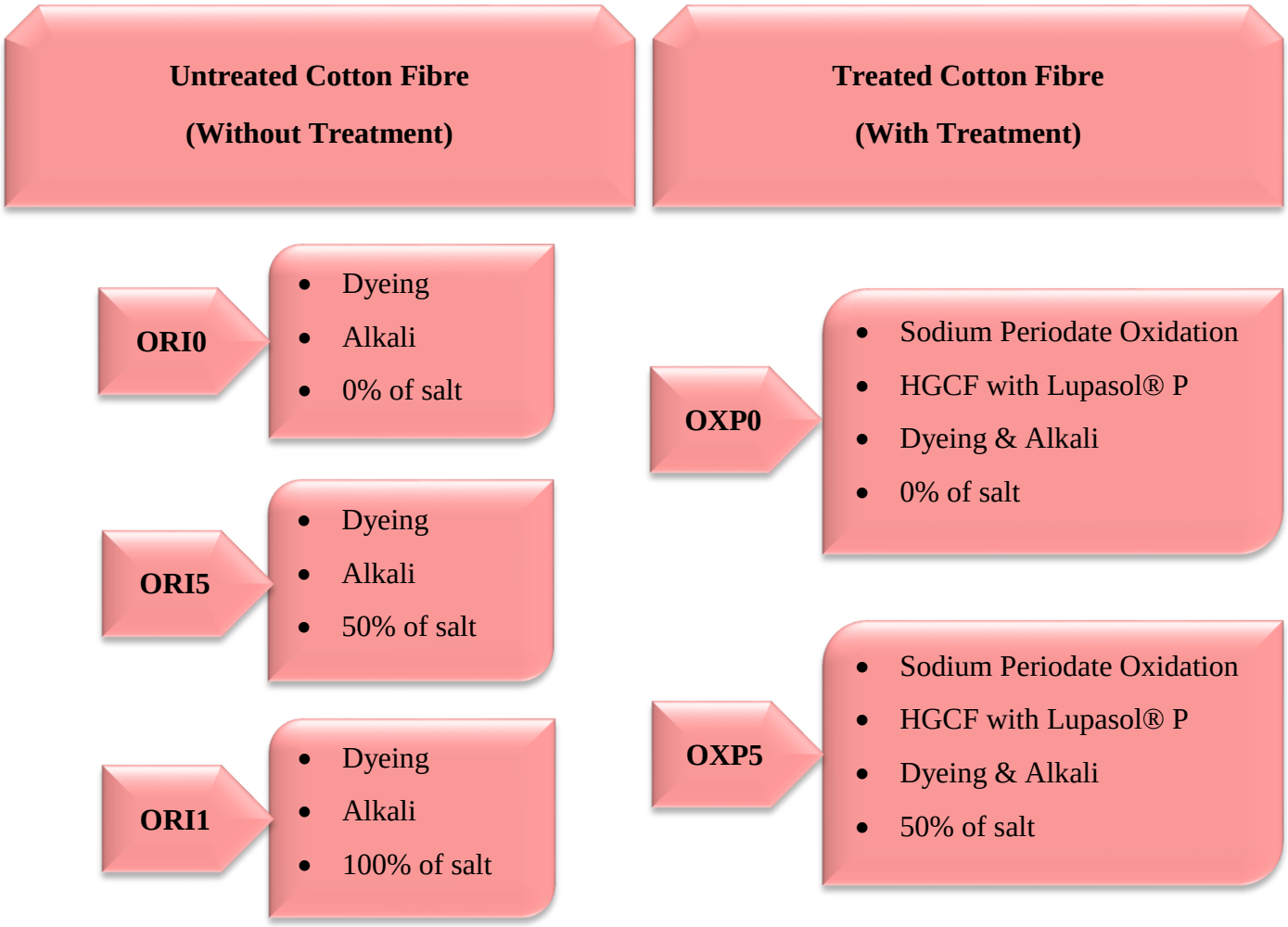
After the oxidation is completed, the oxidized cotton fibre is washed with ice-cold distilled water in the basin to remove the excess oxidant and has to be washed thoroughly. Next, the oxidized cotton samples are dried in the oven at 110 °C for an hour and a half in estimation, until the weight is constant and maintained for characterization. After drying, the samples are placed in the desiccator for one hour before weighting to avoid moisture from the laboratory that affects the weight of the samples as shown in Figure 16. The samples must be weight after oxidation to measure the loss of yield; therefore, the weight of the samples is measured three times to obtain the average. The samples will be further dried in the oven in a shorter time if the weight of the samples is not yet constant.

Figure 16 A desiccator containing the samples

3.3 GRAFTING OF OXIDATED CELLULOSE WITH HYPERBRANCHED POLYMER (LUPASOL® P)

This experiment is divided into untreated and treated cotton fibres. Cotton fibre samples with a size of 21 x 15 cm are prepared under five different conditions as shown in Table 3. Untreated cotton fibre samples will not be treated with oxidation but will only be used for dyeing with different concentrations of salt. Therefore, treated cotton fibre samples are involved in sodium periodate oxidation, HGCF treatment and dyeing with different concentrations of salt. It is necessary to compare the fixing of the dyeing on cotton fibre with and without treatment and with and without salt.

Table 3 Conditions of cotton fibre with its labels.



To calculate the amount of solutions needed for oxidation, grafting and dyeing, the cotton fibres must be weighed first before any treatment is performed. For samples of treated cotton fibre, the sample is immersed in a sodium periodate solution at a concentration of 2 g/L at a liqueur ratio of 30:1. The solution was gently oscillated in the Linitest machine at 40 °C for 60 minutes because it is the optimal condition for sodium periodate oxidation that will be explained in the results and discussion later. The oxidized cotton fibre was then washed several times with cold deionized water to remove the oxidant and was used for the next reaction without drying.

The oxidized cotton fibre was immersed in Lupasol ® P aqueous solution at a concentration of 5 g/L with a liquor ratio of 20:1. The solution was gently oscillated in the Linitest machine at a temperature of 70 °C for 30 minutes. The resulting cotton fibres are then washed several times with deionized water. The resulting cotton fibre was air-dried at room temperature for 24 hours to produce Lupasol® P grafted cotton fibre (HGCF).

3.4 DYEING OF HGCF

The dyeing with reactive dye of treated and untreated cotton fibres is carried out in a dyebath with a liquor ratio of 20:1. A dye concentration of Red Cibacron ZGE is used. The dyebath is prepared by adding the alkali solutions which are sodium carbonate at a concentration of 20 g/L and 30 mL/L of sodium hydroxide 36° Be, sodium sulfate as a salt with concentration of 70 g/L, 3.5 % owf of red reactive dye and dilute the solution with distilled water. The percentage of salt added to the dyebath is based on the conditions set out in Table 3 and the quantity of materials required is shown in Annex 2.

The dyeing of the treated and untreated cotton fibre started at 25 °C and remained in oscillation at this temperature for 5 minutes in the Linitest machine. The temperature then rises steadily to 90 °C in 40 minutes and finally leaves it at a maintained temperature for another 60 minutes, as shown in Figure 16. After colouring, the resulting cotton fabric is thoroughly rinsed and left in hot water at 60 °C. The samples are then soaked in a soap solution of 0.5 g / L Hostapal DTC at a temperature of 95 °C in the Linitest machine for 20 minutes. In the end, the samples are thoroughly rinsed with deionized water and air.

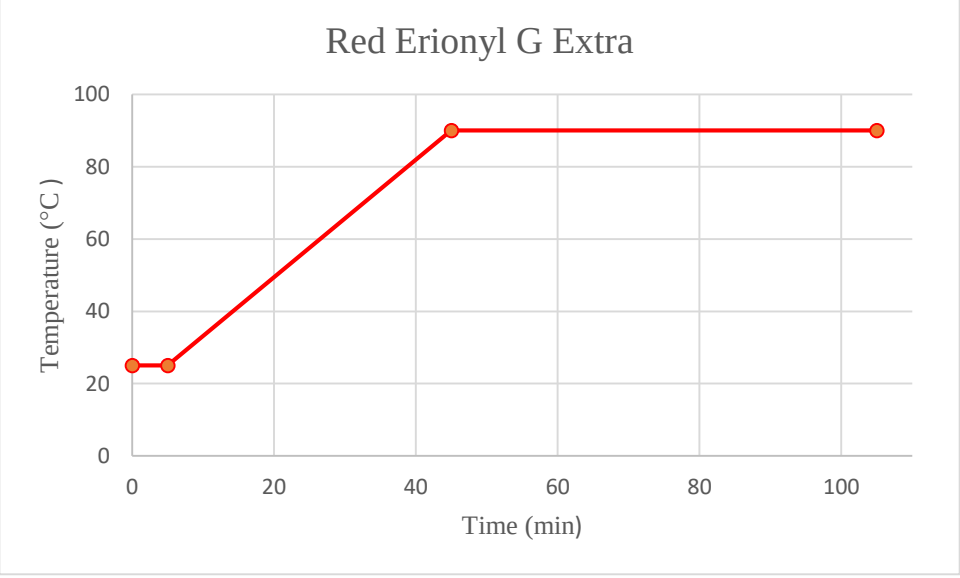


Figure 17 Reaction time of dyeing

3.5 MEASUREMENT

3.5.1 YIELD LOSS

To determine the yield loss of oxidized cotton sample, the direct gravimetric method is applied by using Equation 3:

$$Yield\ loss\ (\%) = \frac{M_0 - M_t}{M_0} \times 100\% \quad (8)$$

Where M_0 and M_t are the absolute dry weights (g) of the samples before and after the oxidation treatment, respectively.[18]

3.5.2 ALDEHYDE GROUP CONTENT

Schiff's base reaction with hydroxylamine hydrochloride, $NH_2OH.HCl$ determines the aldehyde content in periodate-oxidized cotton samples. NaOH titration is used to determine the aldehyde content. Hydrochloric acid is produced from hydroxylamine hydrochloride, and 0.1 M NaOH solution titrates $NH_2OH.HCl$. A 25 g water solution with 1.0 wt % of oxidized fibres is weighted and 5.0 pH adjustment with 0.1 M NaOH solution. The $NH_2OH.HCl$ solution is prepared for 0.05 g / mL hydroxylamine hydrochloride and is also adjusted to pH 5.0 using 0.1 M NaOH. 10mL of $NH_2OH.HCl$ solution is then added to the oxidized fibre that is placed for 4h in a 40 °C heat tub. The titration is done using 0.1 M NaOH, and the quantity of NaOH consumed was recorded when the solution's pH value achieved 5.0. The quantity of the aldehyde is calculated using the following formula:

$$Aldehyde\ Content\ (\%) = \frac{C_1 \times (V_1 - V_2) \times 162}{M \times 1000} \times 100\ \% \quad (9)$$

Where C_1 refers to the concentration of NaOH solution (M), V_1 refers to the quantity of NaOH taken by oxidized fibres (mL), V_2 refers to the quantity of NaOH absorbed by the fibre (mL) and M refers to the weight of the samples (g).[18] The results of aldehyde content in oxidized cotton fibres were collected in the datasheet in Annex 3.

3.5.3 TENSILE STRENGTH

Uster Tansokid tensile testing machine following UNE EN ISO 13934-1 with a load cell of 2500 N as shown in Figure 18 conducted tensile strength measurements of oxidized cotton fibres. The sample test was 15 cm long and 100 mm/min speed. Five original samples of cotton fibres not treated as a reference were tested and compared to oxidized cotton fibres. The samples are left in the laboratory for 24 hours at a temperature of 60 ± 5 °C to adjust the humidity of the samples to eliminate bias before starting the tensile strength test. All information for the resulting measurement of tensile strength comprises of maximum force, Rm, elongation at max break, ε, breaking force, RB, and elongation at break, ε, which was collected in Annex 4.

Figure 18 Uster Tansokid tensile testing machine

3.5.4 FTIR SPECTROSCOPY

IR spectra were obtained between 600 and 4000 cm^{-1} making measurements with 32 scans. The technique is Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Tensor Bruker model 27. The samples were measured by making a previous background and cleaning with ethanol the diamond tip of the equipment in each of the measurements. Measured samples consist of untreated cotton fibre, oxidized cotton fibres with 2 and 4 g/L sodium periodate concentration and HGCF with Lupasol® P.

3.5.5 COLOUR MEASUREMENT

Spectrophotometric readings were carried out using Minolta CM3600 spectrophotometer under standard CIE illuminant D 65. Measurements were performed for a diameter area of 30 mm and a 10° observer. Colour measurements were performed in 4 repetitions for each sample, with the final results calculated as an arithmetic mean and recorded in terms of CIE colorimetric values (L* a* b* C* and h) as well as spectral reflectance varying from 400 nm to 700 nm at 10 nm intervals.

The dyed fabric samples were measured in reflectance (%). The strength of any colorant has to do with the absorption property. The Kubelka – Munk theory gives us the relationship between reflection and absorption:

$$K/S = \frac{(1-R)^2}{2R} \quad (10)$$

Where R is the reflectance, K is absorbance and S is the scattering. By using the above equation colour strength of different samples were measured.

3.5.6 WASHING FASTNESS

Washing fastness test characterizes colour's resistance to fading or running of material following ISO 105-C06: 2010. A textile sample is washed, rinsed and dried sewed with the specified multi-fibre. Grey scales are used to assess the degradation that is attenuating or changing the intensity of the sample colour and the discharge to the multi-fibre. The type of multi-fibre used in this washing speed is ISO 105-F10 TV, consisting of triacetate (CT), cotton (CO), polyamide (PA), polyester (PES), acrylic (PAC) and viscose (CV).

Table 4 The standard condition of washing fastness test

Test Number	Temperature (°C)	Volume of wash bath (mL)	Active chlorine (%)	Sodium perborate (g/L)	Time (min)	N° of steel balls	pH adjustment
C1S	60	50	No	No	30	25	10.5 ± 0.1

Dyed cotton fibre sample is cut in a dimension of 4 x 10 cm and sewed together with the multi-fibre. One multi-fibre is left unsewn to be compared with multi fibre sewn with dyed fabric after the experiment. The standard condition of the washing fastness is referred to in Table 4. In the washing solution, 4 g Hospatal DTC detergent is used for one litre with distilled water. Wash bath is added to each steel container with a volume of 50 mL. The steel balls are then added to the steel container with the amounts of 20 and lastly, the dyed cotton fibre sewed with multi-fibre is added in the steel container including the multi fibre without the dyed cotton fibre. Next, the container is put into Linitest machine filled with water bath which is oscillated with a temperature 60 °C for 30 minutes.

After finishing the time in the Linitest machine, the resulted fabrics are rinsed twice, for one minute at a time, in two different baths of 100 ml of distilled water at 40 °C. The resulted fabrics are then dried in the air at the temperature not more than 60 °C. Finally, the degradation of the colour of resulted dyed cotton fibre is evaluated with grey scale for the degradation by comparing the resulted dyed cotton fibre with the dyed cotton fibre that is not going through the washing fastness. As for the discharge of the colour, the resulted multi-fibre is evaluated with the help of the grey scale for discharge by comparing the multi-fibre sewn with dyed cotton fibre with multi-fibre without dyed cotton fibre.

3.5.7 RUBBING FASTNESS

Rubbing fastness will be determined the fixation of the dyed fabric, against rubbing and discharge on other materials. It is measured in the dry and wet form of the fabric. The rubbing fastness properties of the textile material are measured by comparing the tested fabrics with the grey scale following the rule of UNE-EN ISO 105-X12:2016. The samples of the dyed cotton fibre will be rubbed with white test cloth and unloading it on white test cloth which will be valued with grey scale. The dimensions of the dyed fabric are 5 x 16 cm and white test cloth is 5 x 5 ± 0.2 cm according to ISO 105-F09.

For rubbing fastness in wet form, the white test cloth is soaked completely with distilled water first and ensure the distilled water impregnated the white test cloth by 95 % to 100 %. The white test cloth is put on to grating and stag by steel wire. The dyed cotton fibre is placed flat below the grating with the direction parallel to the movement of the grating. The rubbing counter is set to 10 seconds, which the dyed fabric is rubbed in a straight line 20 times, 10 times in one direction and 10 times in the other. The dyed cotton fibre needs to be placed firmly during the rubbing to avoid slipping. The resulted white test cloth is then removed and dried for 24 hours. Finally, the resulted white test cloth will be proceeding to the evaluation of the discharge on the dyed cotton fibre with the help of the grey scale. The resulted white test cloth is compared with an untested white test cloth.

4 RESULTS AND DISCUSSION

4.1 OPTIMAL CONDITION FOR SODIUM PERIODATE OXIDATION ON THE COTTON FIBRE

The dialdehyde cellulosic fibres from sodium periodate oxidation were obtained in this study. Sodium periodate oxidizes the vicinal hydroxyl groups at C-2 and C-3 in an AGU of cellulose as specific oxidants, thus forming two groups of aldehydes as shown in Figure 19. This study focused on the effect of the sodium periodate dosage on a range of 1 to 4 g/L, the temperature that ranges from 30 °C to 50 °C and reaction time that varies from 10 to 60 minutes.

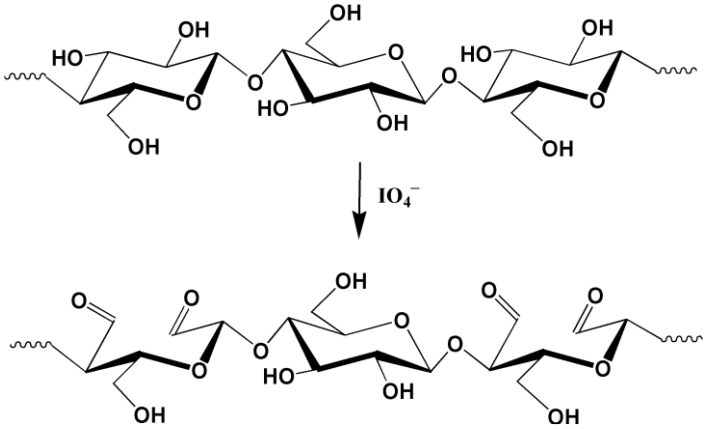


Figure 19 Preparation of oxidized fibre by sodium periodate [18]

4.1.1 YIELD LOSS

A yield loss is measured using the gravimetric method based on Equation (8). The results are presented in a bar chart shown in Figure 20. The bar chart is divided into three columns that consist of different temperatures which are 30 °C, 40 °C and 50 °C with varying the reaction times. The results indicate that at temperature 50 °C, the yield loss is higher. This is due to the possible risk of unstable periodate that decomposes to liberate iodine after some time, which makes it difficult to estimate accurately the amount of periodate consumed. Furthermore, with the oxidative cleavage of the glucopyranose units' bonds between the C-2 and C-3 induced by the oxidation of the sodium periodate, unwanted oxidative or hydrolytic cleavages of glycoside bonds also occurred, leading in yield loss.[18]

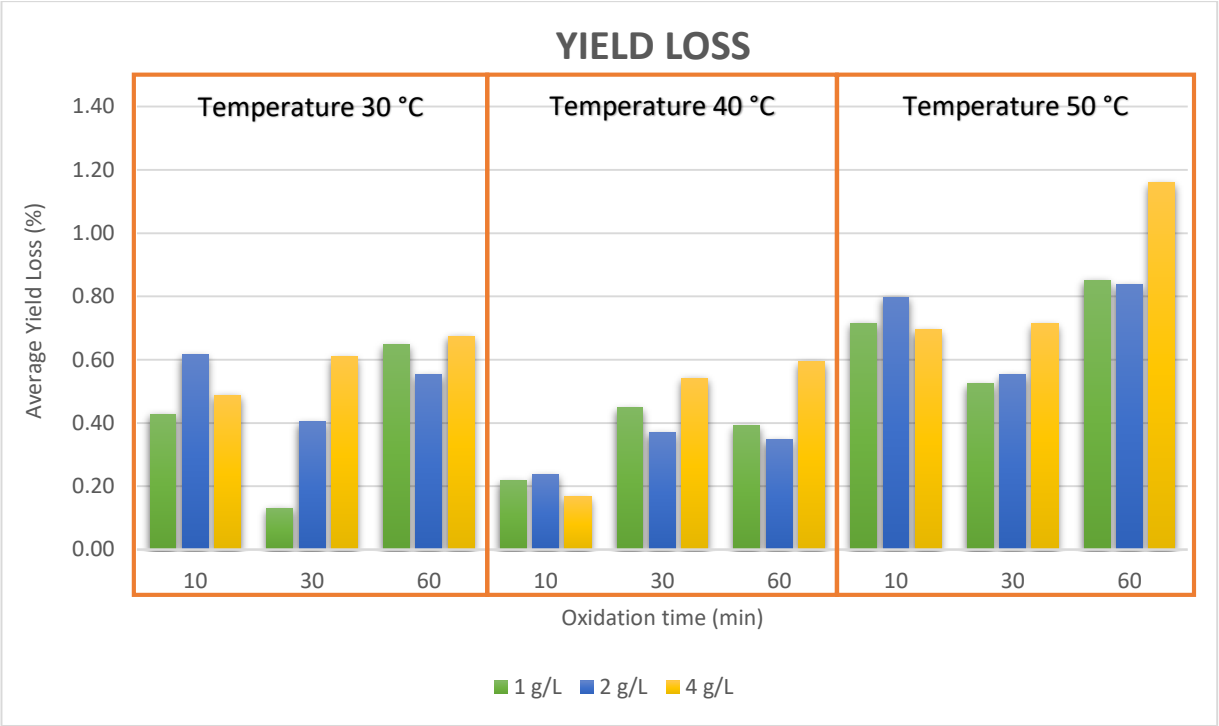


Figure 20 Graph of Average Yield Loss of oxidized cotton fibres

The lowest average yield loss is at a temperature of 40 °C, which can be assumed to be the optimum oxidation temperature, even though, exceptionally, the oxidized cotton fibre in 1 g/L sodium periodate solution at a temperature of 30 °C for 30 minutes has the lowest average yield loss. This may be due to a low concentration of sodium periodate that does not react to AGU cellulose at low temperatures. At temperatures of 40 °C, the average yield loss is at the lowest at oxidation time of 10 minutes but has not been taken into account as an optimal condition because the possibility of cellulose oxidation is not yet fully completed in a short time.

At temperature 40 °C by comparing the oxidation time of 30 and 60 minutes, the sodium periodate concentration of 2 g/L at 60 minutes has the lowest average loss of yield. It can be considered to be an optimal condition, but other factors also need to be considered and cannot conclude the optimal condition by just one factor. The optimal condition can be achieved with the help of these results.

4.1.2 ALDEHYDE CONTENT

The average aldehyde content is measured via sodium hydroxide titration by titrating it with hydroxylamine hydrochloride. The average aldehyde content's results are shown in Figure 21. The sodium periodate concentration played an important role in oxidation reaction because the increase in concentration can result in high aldehyde content which can be seen in the graph. Sodium periodate oxidation of cellulose is a complicated process as it progresses from the amorphous to the crystalline stage. The initial random oxidation occurs in the amorphous cellulose region, followed by the crystallite surface oxidation. For access to the cellulose's internal region, prolonged oxidation times and greater period concentrations may be essential.[3]

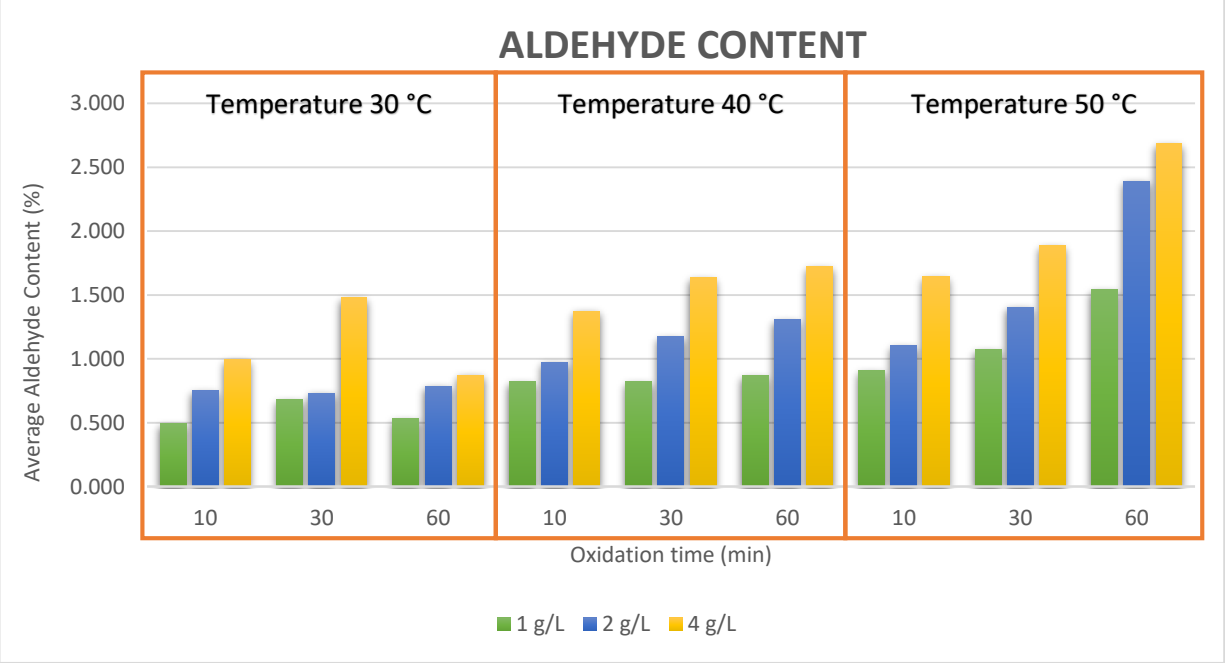


Figure 21 Graph of Aldehyde Content of oxidized cotton fibres

This study used three samples for each condition to find the average of the results which are sample A, B and C. However, only two samples which are B and C are taken into account in finding the average aldehyde content because, during the experiment of sample A, the concentration of NaOH used is too small which is 0.01 M that resulted in inaccurate small readings of titration volume. Hence, the aldehyde content of sample A will not be considered. For sample B and C, 0.1 M NaOH is used for titration that resulted in accepted values of aldehyde content as shown in Annex 3.

Based on the graph, the average aldehyde content is gradually increased as the concentration of sodium periodate increases, with 4 g/L of sodium periodate having the highest aldehyde content at different temperatures and oxidation times. The temperature also affected the increase in aldehyde content, as the average aldehyde content is the highest at 50 °C. The reaction rate between sodium periodate and cellulose is assumed to be faster at high temperatures, which it can take into account when determining the optimal condition for cotton fibre oxidation.

If the oxidation time is compared, the average aldehyde content is higher at 60 minutes, except at a temperature of 30 °C, which can be assumed to be due to poor control of the experiment. By prolonging the oxidation time, the oxidation reagent can react more deeply to the internal area of the cellulose AGU units that will convert to DAC units that can improve the dyeing of the oxidized cotton fibre. If the optimal oxidation condition is determined solely on the basis of aldehyde content, the best condition will be in 4 g/L sodium periodate solution at temperatures of 50 °C for 60 minutes but other factors such as tensile strength of oxidized cotton fibre need to be considered as well, as this condition may affect the mechanical properties of oxidized cotton fibre. For this purpose, the tensile strength of oxidized cotton fibre will be analysed.

4.1.3 TENSILE STRENGTH

Sodium periodate oxidation breaks the crystalline structure of cellulose in the original cotton fibre to some extent, so high aldehyde content can reduce the oxidized cotton fibre's mechanical properties. As the values for untreated cellulose also indicate a loss in tensile strength as shown in Annex 4, the large decreases in tensile strength values could not be entirely due to the stiffness of the cellulose structure by crosslinking. This is related to cellulose's hydrolytic degradation during oxidized cotton fibre preparation.[19] It is well known that when intermolecular crosslinking is given to cotton fabric to increase its crease recovery, the tensile strength of cotton fibre is significantly reduced.[20]

Increasing the quantities of modifying agents and prolonging the oxidation decreases the oxidized fibre's tensile strength compared to unmodified cotton fibres. Reducing the tensile strength of modified fibres can be described by destructive oxidation processes leading to a decrease in polymerization and molecular weight and consequently a decline of mechanical properties.[21] In this study, the tensile strength of the oxidized cotton fibres will be evaluated by its average maximum force. Figure 22 shows the bar chart of the average maximum force of oxidized cotton fibres excluding the original cotton fibres.

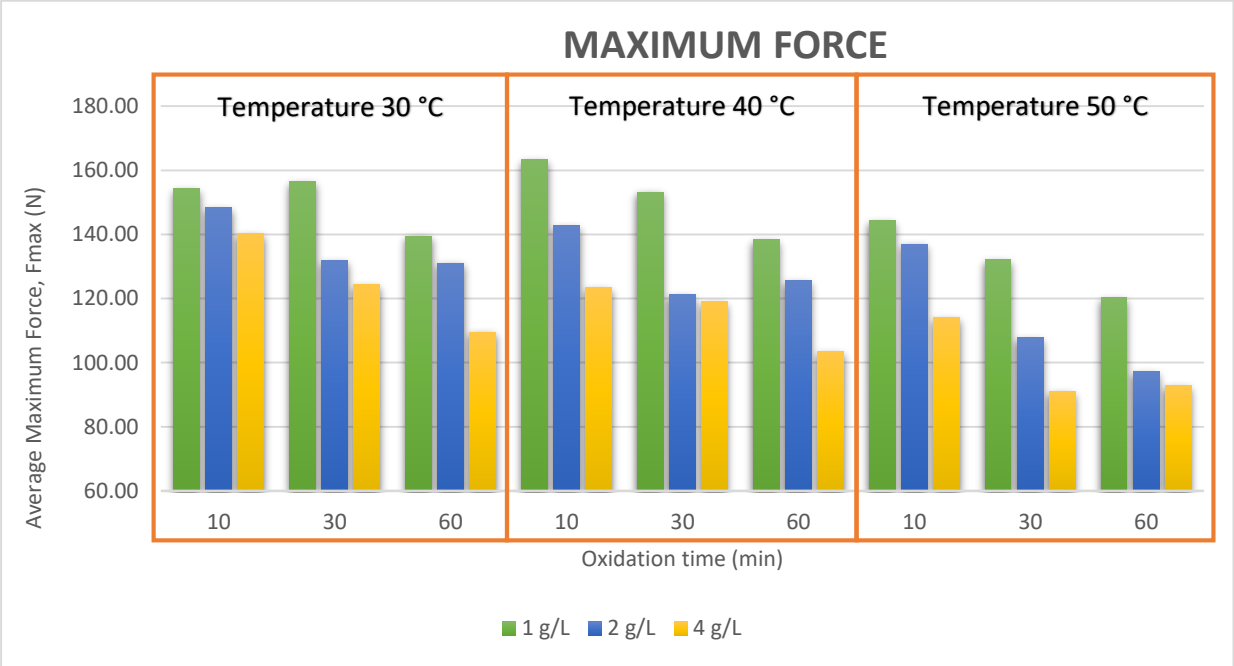


Figure 22 Graph of Maximum Force of oxidized cotton fibres

Five untreated cotton fibres are tested and average maximum force is 180 N as shown in Annex 4 and it will be compared with oxidized cotton fibres on how much is the decrease in tensile strength of the cotton fibres after the treatment. The graph indicates the decrease in average maximum force as the temperature increased. Hence, a very high temperature is not suitable for oxidized cotton fibre as it can weaken the cellulose structure. Based on oxidation time, the longer time will lead to lower average maximum force which is not desired for optimal condition. As the sodium periodate increased, the average maximum force is significantly decreased especially at 4 g/L which can be concluded that high concentration does not necessarily improve the oxidation of cotton fibre.

For oxidized fibre in 1 g/L sodium periodate solution at 40 °C for 10 minutes, the average maximum force is the highest, which reduces the tensile strength of cotton fibre by only 9.4 %. As for the lowest average maximum force, oxidized cotton fibre in 4 g/L sodium periodate solution at 50 °C for 30 minutes reduces the tensile strength of cotton fibre by 49.5 %, which is almost half. Although the average aldehyde content is higher at a temperature of 50 °C, the result is a low tensile strength of cotton fibre. The cotton fabric will deteriorate more quickly and cannot be used in the textile industry in the long term if the cotton fibre has low mechanical properties.

The optimal condition of oxidized cotton fibre based on tensile strength properties has been determined to be at an optimum temperature of 40 °C. At that temperature, the average maximum force is almost the same during the oxidation time, so other factors need to be taken into account. When the sodium periodate concentrations of 1 and 2 g/L are compared, the oxidized cotton fibre of 1 g/L sodium periodate solution has a higher average maximum force. Oxidized cotton fibre with 4 g/L sodium periodate concentration is not taken into account as it results in lower tensile strength. At this point, the optimum condition for oxidized cotton fibre still varies in a few considered conditions and further calculations need to be investigated.

4.1.4 FURTHER CALCULATIONS

As a final solution to find the optimum condition of the oxidized cotton fibre, the strength loss and the multiplication of the average maximum force and the average aldehyde content is calculated. The strength loss is the percentage of a decrease in tensile strength of oxidized cotton fibres from the tensile strength of original cotton fibres and it plays an important role in figuring out the optimal condition of oxidized cotton fibres. The maximum value produced by multiplying the average maximum force and the average aldehyde content signifies the highest values from both factors that can be considered as the optimal condition of the oxidized cotton fibre. All three factors will be studied in the graph of Figure 23 and its data is collected in Annex 5.

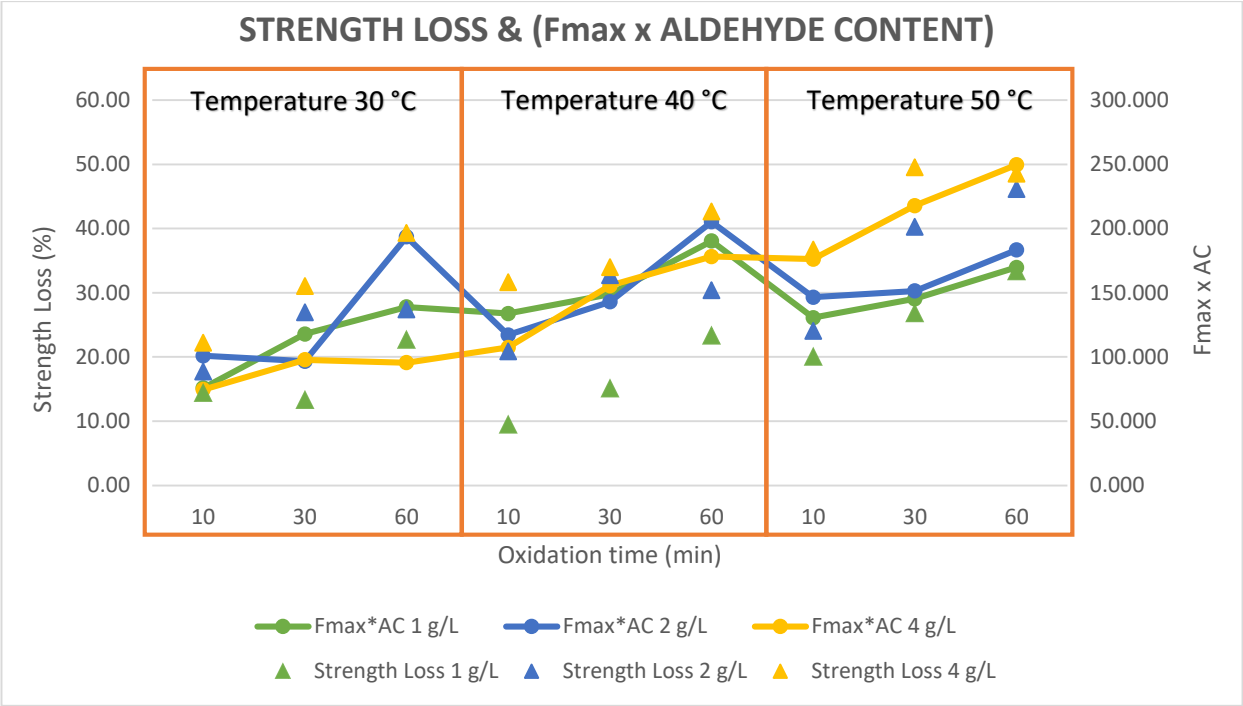


Figure 23 Graph of Strength Loss and Fmax x Aldehyde Content

Line graph of the multiplication of average maximum force (Fmax) and average aldehyde content (AC) needs to be studied first because both factors have a significant effect in oxidation treatment of cotton fibre. The highest value of Fmax x AC is at 50 °C of 4 g/L sodium periodate solution for 60 minutes but this value cannot be considered as optimum because it also has high strength loss which is 48.5 %. The second highest value is also at 50 °C of 4 g/L sodium periodate solution but for 30 minutes but based on the graph, the strength loss of cotton fibre has higher value which is 49.5 % hence it cannot put into consideration. As discussed earlier on the average yield loss part, oxidation treatment at temperature 50 °C produces higher yield loss hence these values cannot take into account as the optimal condition of oxidized cotton fibre.

Next, for the third-highest value of Fmax x AC, the strength loss is significantly low compared to previous which is 30 %. Furthermore, the average yield loss is also quite low which is 0.35 %. As a final decision, the optimal condition for oxidized cotton fibre is 2 g/L sodium periodate solution at 40 °C for 60 minutes. This condition will be used for pre-treatment of cotton fibre which is HCGF treatment and dyeing.

4.2 HGCF WITH LUPASOL® P

The oxidized cotton fibre was immersed in a Lupasol® P aqueous solution during the preparation of HGCF and the resulting aldehyde groups of oxidized cotton fibre would be coupled with Lupasol® P amino groups to generate HGCF.[22] This hyperbranched polymer reaction will contribute significantly to further cotton fibre dyeing, which is why this is an important step in this study.

4.2.1 FTIR ANALYSIS

To determine the variation in functional groups of the unoxidized and oxidized cotton fibres at varying NaIO4 concentrations and also HGCF with Lupasol® P, FTIR spectra were analysed as shown in Figure 24 and 25. In Figure 24, the result of the FTIR analysis showed that after grafting the Lupasol® P to the fabric, a change in chemical composition occurred. OH bending vibration forming hydrogen bonds in the cellulose molecule is ascribed to the wider absorption band between 3000 and 3600 cm^{-1}. This common absorption band consists of two tiny vibrations at 3296 cm^{-1} attributed to intermolecular bonds of hydrogen and 3341 cm^{-1} ascribed to intra-molecular bonds of hydrogen. The peaks at 2895-2908 cm^{-1}, ascribed to asymmetric vibrations of $–CH_2$, were noted. [2]

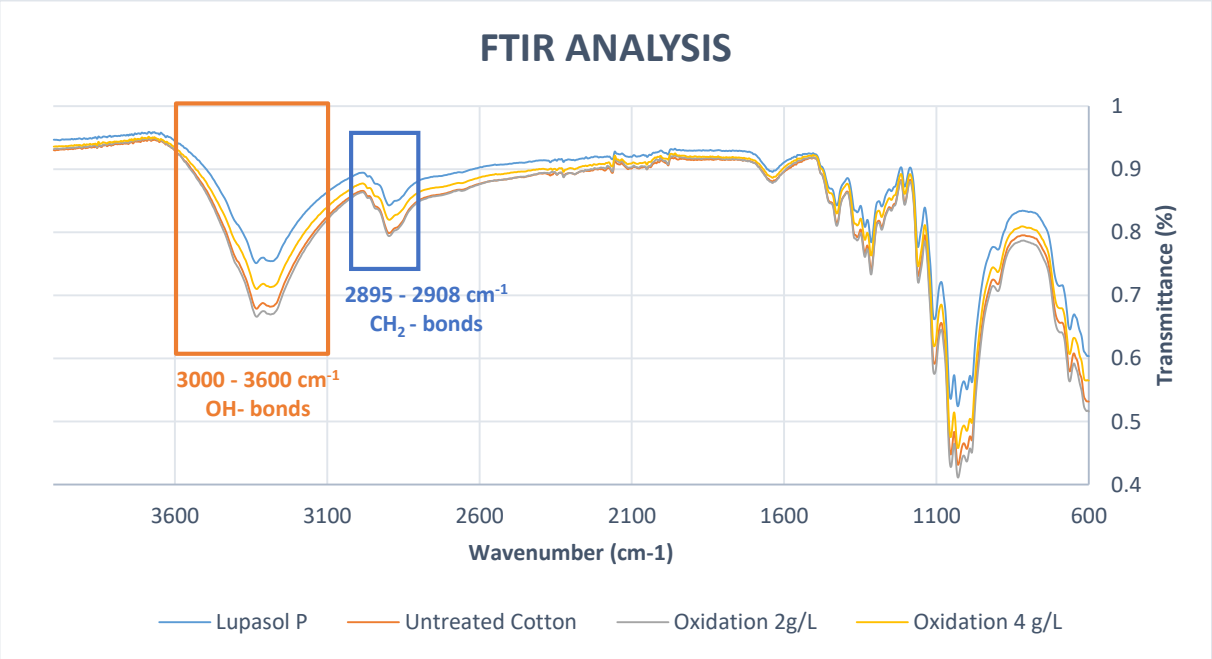


Figure 24 FTIR Analysis

In Figure 25, 1072 cm^{-1} absorption peaks were associated with the C-O-C group's anti-symmetric stretching vibrations. The cyclic hemiacetal linkage resulted in the presence of broadband at 887-895 cm^{-1}. The characteristic absorption band C=O double bond of aldehyde groups was present at 1720–1740 cm^{-1} after oxidation, confirming that aldehyde groups were successfully introduced through sodium periodate oxidation to the surface of cotton fibres. The absorption peak in the HGCF's IR spectrum at 1640-1569 cm^{-1} corresponds to the primary amine N-H bending in Lupasol® P.[8][18]

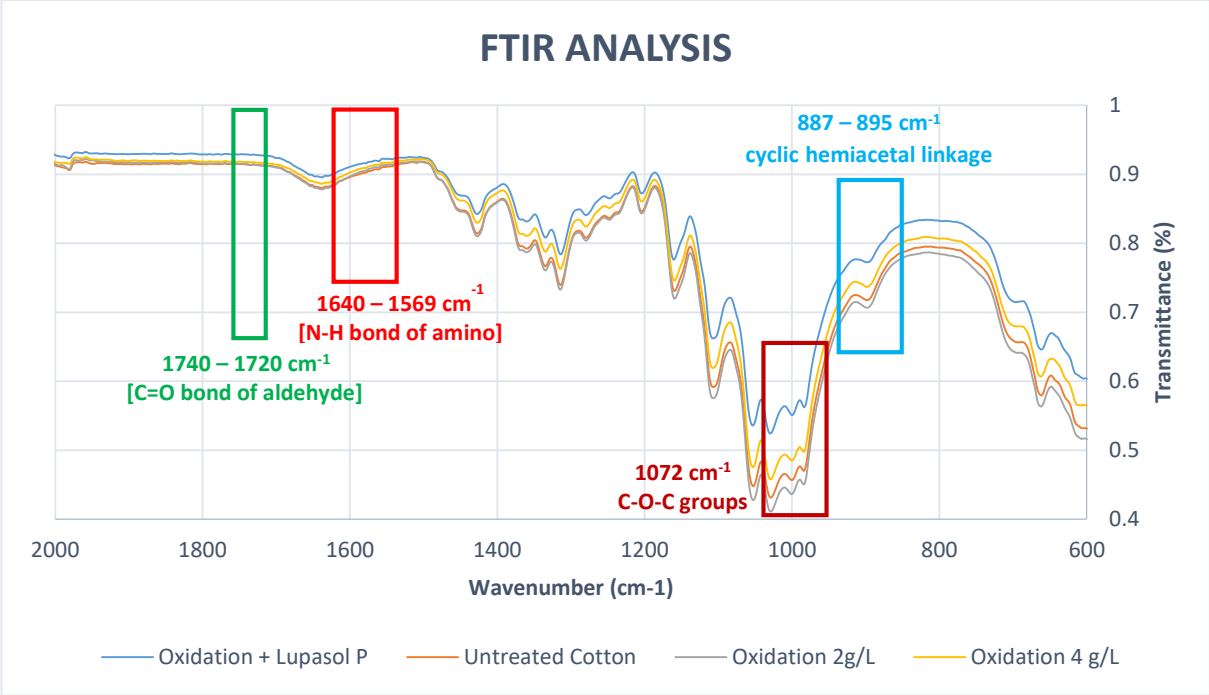


Figure 25 FTIR Analysis

4.3 DYEING OF HGCF

At the end of this study, untreated and treated cotton fibres are dyed with reactive red dyes to observe the dye fixation on cotton fibres. Besides, this experiment is also important to identify the difference in the usage of salt during dyeing of untreated and treated cotton fibres. Polyethyleneimines from Lupasol® P will generate amine groups that act as cationic site in treated cotton. Therefore, dye molecules being an anionic site are attracted towards the fibre when dyed in the presence of alkali which reduces the requirement of salt during dyeing.[23]

4.3.1 COLOUR STRENGTH (K/S VALUE) OF COTTON FIBRE

The colour strength (K/S) is used to express the reflectance-based reduction ratio of the light owning to the absorption and dispersion achieved. The higher the colour strength the more dye is fixed on the fabric and the effect of low dye variation will be on the fabric because light is more reflected in a uniform surface.[2] Figure 26 showed the graph of K/S value of five cotton fibres that have passed through different conditions. Table 3 explains the name of the samples, and Annex 6 presents the data.

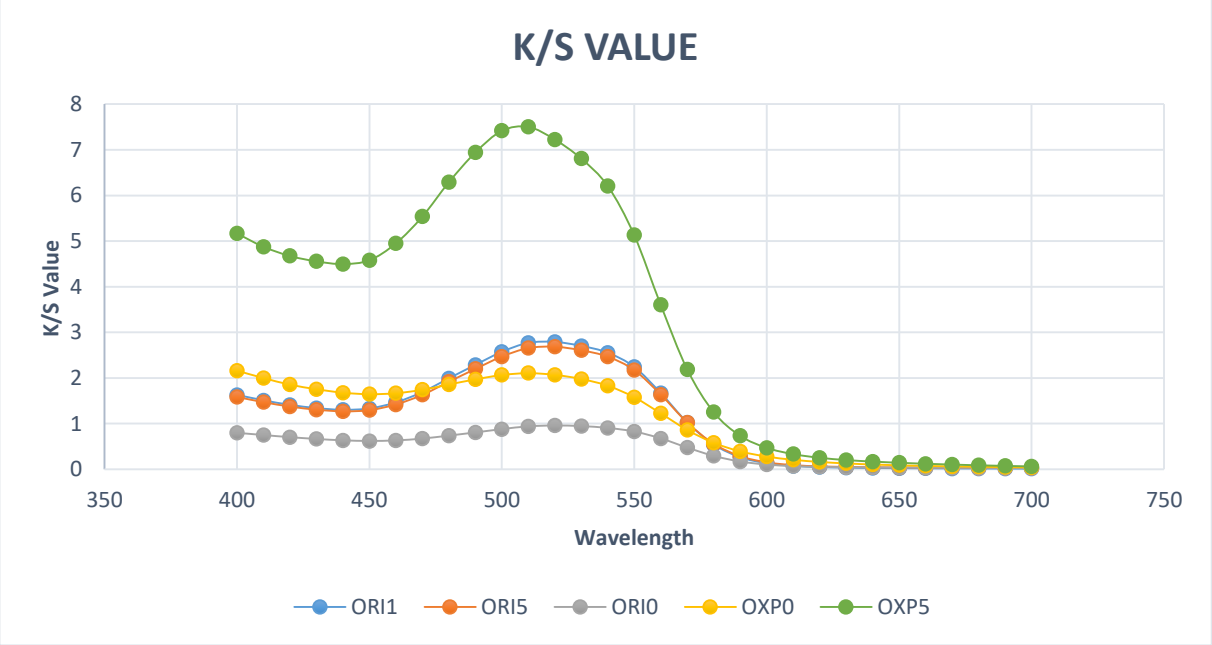


Figure 26 Graph of K/S Value of cotton fibre

Based on the graph in Figure 26, the most significant value compared with other samples' values is the sample OXP5 which is the treated cotton fibre with 50 % salt concentration. Compared to untreated cotton fibre with 50 % salt concentration, the maximum K/S value shown in Table 5 has increased by 64 %. This proves that by the pre-treatment of cotton fibre, the fixation of dye on cotton has improved significantly. The pre-treatment of cotton fibre is therefore important for the dyeing industry to reduce highly coloured environmental effluent. Increased K/S value in cotton fibre treated with oxidation and grafted hyperbranched polymer points to the existence of a higher amount of dye absorbed in the treated fabric. It is also confirmed that the yield of colour in cationized cotton fibre was improved compared to untreated cotton fibre.

For untreated cotton fibre with a concentration of 100% salt, which is ORI1, its maximum K/S value is also lower than OXP5 and similar to ORI5, which means that the use of salt in dyeing can be reduced by pre-treatment of cotton fibre. When comparing untreated and treated cotton fibres with no salt solution which are ORI0 and OXP0, there is a clear difference in K/S values, which is increased by 55%. However, the K/S value of cotton fibre with no salt solution is still lower than that of cotton fibre with a salt solution, which shows that salt is quite important in the dyeing process, but a reduction in salt is needed to save the environment.

The ORI1 and OXP0 samples are compared to perform a dyeing process without any salt involved. The maximum K/S value obtained from this experiment shows that ORI1 and OXP0 are almost the same, but the maximum K/S value of OXP0 is slightly lower than ORI1. This indicated that a reduction in the concentration of salt in the dyeing process is possible with the aid of pre-treatment of cotton fibre.

Table 5 Maximum K/S Value and Colour Difference

Sample		Maximum K/S Value	Colour Difference
Untreated Cotton Fibres	**ORI1**	2.7902	Reference
	ORI5	2.687	2.5627
	ORI0	0.9581	19.3471
Treated Cotton Fibres	**OXP0**	2.1619	14.3131
	OXP5	7.5041	15.823

The colour difference was studied using the CIELAB system and the results are shown in Table 5 where untreated cotton fibre with a 100 % salt concentration is used as a reference. The data for L*, a* and b* are collected in Annex 6. The colour difference is quite high for all samples except for ORI5 and the more obvious colour difference for all samples was shown in Figure 27. The OXP5 sample is more reddish, while the other samples are more pink, which explains the very effective fixation of the red reactive dye for OXP5. The difference in colour can also be explained by the addition of salt in the dyeing process when cotton fibres with no salt concentration are compared with cotton fibres with salt concentration, both have different shades of colour.

Figure 27 Cotton Fibres after Dyeing

4.3.2 WASHING FASTNESS

Washing fastness is tested for the colour change and staining of reactive dyed of untreated and treated cotton fibres after dyeing by using the standard grey scale reading. The results are presented in Table 6 which consists of the degradation and staining of the cotton fibre. Cotton fibre of OXP5 produced a great result in dye fixation and, when compared with ORI1 and ORI5, the results of degradation and staining results are almost similar. It can be assumed that the pre-treatment of cotton fibre and the reduction of salt concentrations do not affect the degradation and staining of the cotton fibre. This may be due to the formation of strong ionic bond between the fibre and the dye because it is just as good as the covalent bond that normally binds the dye and cotton fibre.

The degradation of the OXP5 is graded as regular while the staining on cotton and viscose is graded as very bad, similar to ORI1 and ORI5. In general, the exhaustion of dyeing needs to be further studied to avoid the production of bad stain cotton fibre. The OXP0 sample has a better grade than ORI1 in terms of degradation and staining, which is a good sign of improving the salt-free dyeing process.

Table 6 Results of washing fastness

Washing	Degradation	Staining					
		Triacetate (CT)	Cotton (CO)	Polyamide (PA)	Polyester (PES)	Acrylic (PAC)	Viscose (CV)
ORI0	3-4	4-5	2	3	4-5	5	2-3
ORI1	2-3	4	1-2	3	3-4	4	1-2
ORI5	3	3	1	2	4	4-5	1-2
OXP0	3-4	4-5	1-2	3	4-5	4-5	2
OXP5	3	3-4	1	2	3	3-4	1-2

Index of the Gray Scale:

5 – Very good / excellent

4 – Good

3 – Medium / regular

2 – Bad / Deficient

1 – Very bad

4.3.3 RUBBING FASTNESS

Rubbing fastness is a basic test used to determine the quality of coloured fabric. The purpose of this test is to determine the amount of colour transferred by rubbing from the surface of coloured textile materials to the other surface. The test consists of wet and dry conditions and the results are shown in Table 7. The result shows that the dry rubbing fastness of all samples did not change and all samples scored very good grade. This may be due to the formation of strong ionic bond between the anionic dye molecule and the cationic cotton surface.

The results of wet rubbing fastness are also graded as good but not as good as the dry condition. This may be due to the tendency of the hydrolysed dyes being able to form hydrogen bonds with amino group on the cotton surface. For this test, the results of OXP5 compared with ORI1 and ORI5 are quite the same hence it can be concluded that the pre-treatment of cotton fibre does not affect the staining properties of the cotton fibre. Also, the sample of OXP0 produced a quite similar grade with ORI1.

Table 7 Results of Rubbing fastness

Rubbing fastness		**Staining**	
		Dry	**Wet**
Untreated Cotton Fibre	**ORI1**	5	3-4
	ORI5	4-5	4
	ORI0	5	4-5
Treated Cotton Fibre	**OXP0**	4-5	4
	OXP5	4-5	3-4

Index of the Gray Scale:

5 – Very good / excellent

4 – Good

3 – Medium / regular

2 – Bad / Deficient

1 – Very bad

5 BUDGET OF THE EXPERIMENT

This study consists of four main experiments that require a budget for each experiment in which materials, including chemicals, are used in the laboratory to carry out the experiment. The experiments involved are sodium periodate oxidation, HGCF and dyeing, washing fastness and rubbing fastness as shown in Table 8. For the experiments of sodium periodate oxidation and HCGF and dyeing, the overall process of the experiment is considedred to be one cost while washing fastness and rubbing fastness' cost are for each sample. The total budget used in this experiment is 469 €.

Table 8 Budget of the Experiment

Experiment	Cost (€)	No. of Sample	Total Cost (€)
Sodium Periodate Oxidation	72 / process	-	72
HGCF and Dyeing	72 / process	-	72
Washing Fastness	32 / sample	5	160
Rubbing Fastness	33 / sample	5	165
		Total Budget (€)	469

6 CONCLUSION

This study is an evaluation to determine the optimal conditions for sodium periodate oxidation and the effect of Lupasol ® P hyperbranched polymer grafting on the salt-free cotton fibre dyeing process. Sodium periodate oxidation, together with some morphological changes of cotton fibres, allows unique chemical modifications under aqueous and moderate conditions. The cotton fibre was oxidized by a sodium periodate oxidation reaction to dialdehyde cellulose. By adjusting the sodium periodate concentration, temperature and oxidation time, the cotton fibre is oxidized under different conditions.

The optimal condition of oxidized cotton fibre in this study is at temperature 60 °C for 60 minutes with 2 g/L sodium periodate concentration where the yield loss is only 0.35 %, the aldehyde content is 1.635 % and the tensile strength is 125.59 N which the strength loss is only 30 %. Not all the values from the optimal condition are the maximum values obtained, hence the optimum conditions for oxidized cotton fibre did not have to be the highest amount if all the factors are taken into account. A mild oxidation had no important impact on the mechanical properties, whereas cotton fibre's mechanical properties declined significantly with increased amount of sodium periodate and prolonged oxidation time.

Hyperbranched polymer grafted cotton fibre (HGCF) with Lupasol® P was obtained by reaction between the aldehyde groups on the oxidized cotton fibre and the amino groups of Lupasol® P. HGCF prepared under optimum conditions and dyed with red reactive dyes under five distinct conditions yielded significantly increased colour strength (K/S) for the 50 % salt concentration of treated cotton fibre. It demonstrates that using pre-treatment can reduce the use of salt in the dyeing process. To achieve a salt-free dyeing process by applying oxidation and hyperbranched polymer grafting, the salt-free treated cotton fibre is shown to improve its K/S value compared to the salt-free untreated cotton fibre. Also, its K/S value is nearly similar to untreated cotton fibre with 100% salt concentration, which demonstrates a high possibility of executing the salt-free dyeing process.

A comparative of reactive dyed untreated and treated cotton fibres were also obtained for the properties of washing fastness and rubbing fastness. The results from grey scale readings indicate very excellent grade of degradation and staining properties for both washing and rubbing fastness for both reactive dyed of untreated and treated cotton fibre. It proves that cotton fibre pre-treatment does not alter cotton fibre's staining properties.

Based on all achieved results of this study, it was revealed that cotton fabric after pre-treatment can be dyed with environmentally friendly reactive dyes without any use of salt during its dyeing and thus can cut down the dye effluent load. Cationization treatment of cotton for improved dyeability and reduction of salt concentration in the dyeing process provide enormous scope for further investigation to suit today’s need for greener technology.

7 RECOMMENDATIONS

There are a few recommendations that can be considered after this experiment has been carried out. Since sodium periodate is harmful to the environment, further studies are needed to discover new oxidizing agents that can replace sodium periodate, which has the same chemical modification as sodium periodate. The recyclability of excess sodium periodate is also possible if further investigation is carried out. Based on the general Lupasol® datasheet, Lupasol® is toxic to aquatic life with a long-lasting effect. Further studies on different polymers with a high amino group density such as Lupasol® may also help to reduce environmental damage.

The results of the K/S value show that the sample OXP5 has a huge difference to the sample ORI1, thus achieving the K/S value of ORI1, but a reduction in the salt concentration can be discovered using pre-treatment of cotton fibre. This is to see how much salt concentration can be reduced to produce the same results, but with both reactive dyed of untreated and treated cotton fibre.

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9 ANNEXES

ANNEXE 1: BEFORE AND AFTER OXIDATION TREATMENT

BEFORE OXIDATION TREATMENT: SAMPLE A

Sample	Time, t (min)	Temperature, T (°C)	Concentration of periodate, [NaIO4] (g/L)	Absolute dry weights of the samples before the oxidation treatment, Mo (g)			Solution of sodium periodate used (mL)
				1st reading	2nd reading	Average	
A.10.30.1	10	30	1	1.045	-	1.045	31.4
A.10.30.2	10	30	2	1.0665	-	1.0665	32
A.10.30.4	10	30	4	1.0525	-	1.0525	31.6
A.30.30.1	30	30	1	1.1307	-	1.1307	34
A.30.30.2	30	30	2	1.043	-	1.043	31.3
A.30.30.4	30	30	4	1.03	-	1.03	30.3
A.60.30.1	60	30	1	1.0872	-	1.0872	32.6
A.60.30.2	60	30	2	1.0668	-	1.0668	32
A.60.30.4	60	30	4	1.0403	-	1.0403	31.2
A.10.40.1	10	40	1	1.0092	1.0119	1.01055	30.3
A.10.40.2	10	40	2	1.0561	1.0558	1.05595	31.7
A.10.40.4	10	40	4	1.0375	1.0382	1.03785	31.1
A.30.40.1	30	40	1	1.0556	1.0526	1.0541	31.6
A.30.40.2	30	40	2	1.0451	1.0426	1.04385	31.3
A.30.40.4	30	40	4	1.0795	1.0744	1.07695	32.3
A.60.40.1	60	40	1	1.0701	1.0695	1.0698	32.1
A.60.40.2	60	40	2	1.0962	1.0951	1.09565	32.9
A.60.40.4	60	40	4	1.0754	1.0712	1.0733	32.2
A.10.50.1	10	50	1	1.0466	1.0538	1.0502	31.5
A.10.50.2	10	50	2	1.0538	1.0541	1.05395	31.6
A.10.50.4	10	50	4	1.007	1.0078	1.0074	30.2
A.30.50.1	30	50	1	1.0717	1.0759	1.0738	32.2
A.30.50.2	30	50	2	1.1118	1.1174	1.1146	33.4
A.30.50.4	30	50	4	1.0214	1.0246	1.023	30.7
A.60.50.1	60	50	1	1.0585	1.0599	1.0592	31.8
A.60.50.2	60	50	2	1.0306	1.0374	1.034	31
A.60.50.4	60	50	4	1.0665	1.0662	1.06635	32

BEFORE OXIDATION TREATMENT: SAMPLE B

Sample	Time, t (min)	Temperature, T (°C)	Concentration of periodate, [NaIO4] (g/L)	Absolute dry weights of the samples before the oxidation treatment, Mo (g)			Solution of sodium periodate used (mL)
				1st reading	2nd reading	Average	
B.10.30.1	10	30	1	1.0382	1.0375	1.03785	31.14
B.10.30.2	10	30	2	1.0544	1.0535	1.05395	31.62
B.10.30.4	10	30	4	1.0559	1.0549	1.0554	31.66
B.30.30.1	30	30	1	1.0373	1.0371	1.0372	31.12
B.30.30.2	30	30	2	1.0270	1.0256	1.0263	30.79
B.30.30.4	30	30	4	0.9945	0.9917	0.9931	29.79
B.60.30.1	60	30	1	1.0065	1.0069	1.0067	30.20
B.60.30.2	60	30	2	1.0975	1.0946	1.09605	32.88
B.60.30.4	60	30	4	1.0400	1.0397	1.0399	31.20
B.10.40.1	10	40	1	1.0348	1.0386	1.0367	31.10
B.10.40.2	10	40	2	1.0281	1.0290	1.02855	30.86
B.10.40.4	10	40	4	1.0244	1.0296	1.027	30.81
B.30.40.1	30	40	1	1.0271	1.0320	1.02955	30.89
B.30.40.2	30	40	2	1.0219	1.0245	1.0232	30.70
B.30.40.4	30	40	4	1.0346	1.0337	1.03415	31.02
B.60.40.1	60	40	1	1.0450	1.0424	1.0437	31.31
B.60.40.2	60	40	2	1.0486	1.0490	1.0488	31.46
B.60.40.4	60	40	4	1.0300	1.0280	1.0290	30.87
B.10.50.1	10	50	1	1.0299	1.028	1.02895	30.87
B.10.50.2	10	50	2	1.0592	1.0552	1.0572	31.72
B.10.50.4	10	50	4	1.046	1.0432	1.0446	31.34
B.30.50.1	30	50	1	1.015	1.0124	1.0137	30.41
B.30.50.2	30	50	2	1.0317	1.0249	1.0283	30.85
B.30.50.4	30	50	4	1.0412	1.0411	1.04115	31.23
B.60.50.1	60	50	1	1.0609	1.0712	1.06605	31.98
B.60.50.2	60	50	2	1.0369	1.0315	1.0342	31.03
B.60.50.4	60	50	4	1.0549	1.0515	1.0532	31.60

BEFORE OXIDATION TREATMENT: SAMPLE C

Sample	Time, t (min)	Temperature, T (°C)	Concentration of periodate, [NaIO4] (g/L)	Absolute dry weights of the samples before the oxidation treatment, Mo (g)			Solution of sodium periodate used (mL)
				1st reading	2nd reading	Average	
C.10.30.1	10	30	1	1.0645	1.0600	1.06225	31.87
C.10.30.2	10	30	2	1.0639	1.0603	1.0621	31.86
C.10.30.4	10	30	4	1.0630	1.0596	1.0613	31.84
C.30.30.1	30	30	1	1.0485	1.0465	1.0475	31.43
C.30.30.2	30	30	2	1.0530	1.0507	1.0519	31.56
C.30.30.4	30	30	4	1.0412	1.0407	1.04095	31.23
C.60.30.1	60	30	1	1.0592	1.0603	1.05975	31.79
C.60.30.2	60	30	2	1.0354	1.0344	1.0349	31.05
C.60.30.4	60	30	4	1.0322	1.0287	1.03045	30.91
C.10.40.1	10	40	1	1.0598	1.0583	1.05905	31.77
C.10.40.2	10	40	2	1.0459	1.0431	1.0445	31.34
C.10.40.4	10	40	4	1.0486	1.0427	1.04565	31.37
C.30.40.1	30	40	1	1.0888	1.0937	1.09125	32.74
C.30.40.2	30	40	2	1.0979	1.0948	1.09635	32.89
C.30.40.4	30	40	4	1.0736	1.0713	1.07245	32.17
C.60.40.1	60	40	1	1.0286	1.027	1.0278	30.83
C.60.40.2	60	40	2	1.0392	1.0398	1.0395	31.19
C.60.40.4	60	40	4	1.0416	1.041	1.0413	31.24
C.10.50.1	10	50	1	1.0711	1.0615	1.0663	31.99
C.10.50.2	10	50	2	1.0475	1.0395	1.0435	31.31
C.10.50.4	10	50	4	1.0755	1.0688	1.07215	32.16
C.30.50.1	30	50	1	1.0816	1.0728	1.0772	32.32
C.30.50.2	30	50	2	1.0519	1.055	1.05345	31.60
C.30.50.4	30	50	4	1.0869	1.0873	1.0871	32.61
C.60.50.1	60	50	1	1.0623	1.0664	1.06435	31.93
C.60.50.2	60	50	2	1.0929	1.0929	1.0929	32.79
C.60.50.4	60	50	4	1.0336	1.033	1.0333	31.00

AFTER OXIDATION TREATMENT: SAMPLE A

Sample	Time, t (min)	Temperature, T (°C)	Concentration of periodate, [NaIO4] (g/L)	Absolute dry weights of the samples after the oxidation treatment, M_t (g)			
				1st reading	2nd reading	3rd reading	Average
A.10.30.1	10	30	1	1.0386	1.0349	1.0405	1.0380
A.10.30.2	10	30	2	1.0531	1.0409	1.0521	1.0487
A.10.30.4	10	30	4	1.0394	1.0403	1.0435	1.0411
A.30.30.1	30	30	1	1.1262	1.1255	1.1284	1.1267
A.30.30.2	30	30	2	1.0343	1.0353	1.0345	1.0347
A.30.30.4	30	30	4	1.0171	1.018	1.0186	1.0179
A.60.30.1	60	30	1	1.086	1.0776	1.0773	1.0803
A.60.30.2	60	30	2	1.0638	1.0553	1.055	1.0580
A.60.30.4	60	30	4	1.0333	1.0265	1.0238	1.0279
A.10.40.1	10	40	1	1.0116	1.005	1.0115	1.0094
A.10.40.2	10	40	2	1.0544	1.0539	1.0533	1.0539
A.10.40.4	10	40	4	1.0415	1.0383	1.0335	1.0378
A.30.40.1	30	40	1	1.058	1.0526	1.0491	1.0532
A.30.40.2	30	40	2	1.0477	1.0403	1.038	1.0420
A.30.40.4	30	40	4	1.0774	1.0721	1.0674	1.0723
A.60.40.1	60	40	1	1.0696	1.0669	1.0669	1.0678
A.60.40.2	60	40	2	1.0961	1.0944	1.0918	1.0941
A.60.40.4	60	40	4	1.07	1.0699	1.0641	1.0680
A.10.50.1	10	50	1	1.0427	1.0467	1.0493	1.0462
A.10.50.2	10	50	2	1.0446	1.0494	1.051	1.0483
A.10.50.4	10	50	4	1.0042	1.0069	1.0057	1.0056
A.30.50.1	30	50	1	1.0733	1.0691	1.0713	1.0712
A.30.50.2	30	50	2	1.1127	1.1058	1.1079	1.1088
A.30.50.4	30	50	4	1.0225	1.0188	1.0173	1.0195
A.60.50.1	60	50	1	1.0582	1.0543	1.051	1.0545
A.60.50.2	60	50	2	1.0307	1.0301	1.0264	1.0291
A.60.50.4	60	50	4	1.0611	1.0567	1.0561	1.0580

AFTER OXIDATION TREATMENT: SAMPLE B

Sample	Time, t (min)	Temperature, T (°C)	Concentration of periodate, [NaIO4] (g/L)	Absolute dry weights of the samples after the oxidation treatment, M_t (g)			
				1st reading	2nd reading	3rd reading	Average
B.10.30.1	10	30	1	1.037	1.0367	1.035	1.0362
B.10.30.2	10	30	2	1.0544	1.0524	1.0503	1.0524
B.10.30.4	10	30	4	1.0576	1.0522	1.0497	1.0532
B.30.30.1	30	30	1	1.0419	1.0331	1.0365	1.0372
B.30.30.2	30	30	2	1.0275	1.018	1.0218	1.0224
B.30.30.4	30	30	4	0.9893	0.9865	0.9859	0.9872
B.60.30.1	60	30	1	1.0023	1.0009	0.9981	1.0004
B.60.30.2	60	30	2	1.0876	1.0847	1.0902	1.0875
B.60.30.4	60	30	4	1.0327	1.0302	1.036	1.0330
B.10.40.1	10	40	1	1.032	1.0341	1.0278	1.0313
B.10.40.2	10	40	2	1.0248	1.0282	1.0201	1.0244
B.10.40.4	10	40	4	1.0241	1.0226	1.0192	1.0220
B.30.40.1	30	40	1	1.0201	1.0232	1.0197	1.0210
B.30.40.2	30	40	2	1.0174	1.0154	1.0134	1.0154
B.30.40.4	30	40	4	1.0312	1.0369	1.0283	1.0321
B.60.40.1	60	40	1	1.0434	1.049	1.0381	1.0435
B.60.40.2	60	40	2	1.049	1.0509	1.0442	1.0480
B.60.40.4	60	40	4	1.0236	1.0283	1.0225	1.0248
B.10.50.1	10	50	1	1.0265	1.0177	1.0164	1.0202
B.10.50.2	10	50	2	1.0541	1.0459	1.0459	1.0486
B.10.50.4	10	50	4	1.0420	1.0356	1.0336	1.0371
B.30.50.1	30	50	1	1.0141	1.0078	1.0058	1.0092
B.30.50.2	30	50	2	1.0276	1.0228	1.0325	1.0276
B.30.50.4	30	50	4	1.0418	1.0349	1.0234	1.0334
B.60.50.1	60	50	1	1.0558	1.0522	1.0527	1.0536
B.60.50.2	60	50	2	1.0245	1.0220	1.0226	1.0230
B.60.50.4	60	50	4	1.0400	1.0382	1.0360	1.0381

AFTER OXIDATION TREATMENT: SAMPLE C

Sample	Time, t (min)	Temperature, T (°C)	Concentration of periodate, [NaIO4] (g/L)	Absolute dry weights of the samples after the oxidation treatment, M_t (g)			
				1st reading	2nd reading	3rd reading	Average
C.10.30.1	10	30	1	1.0583	1.0574	1.0566	1.0574
C.10.30.2	10	30	2	1.0634	1.061	1.0609	1.0618
C.10.30.4	10	30	4	1.0636	1.0591	1.0559	1.0595
C.30.30.1	30	30	1	1.0506	1.0461	1.0447	1.0471
C.30.30.2	30	30	2	1.0517	1.0516	1.0513	1.0515
C.30.30.4	30	30	4	1.0459	1.0378	1.0371	1.0403
C.60.30.1	60	30	1	1.0531	1.0514	1.053	1.0525
C.60.30.2	60	30	2	1.0342	1.0345	1.0343	1.0343
C.60.30.4	60	30	4	1.0302	1.0288	1.0272	1.0287
C.10.40.1	10	40	1	1.0632	1.0575	1.0561	1.0589
C.10.40.2	10	40	2	1.0433	1.0430	1.0435	1.0433
C.10.40.4	10	40	4	1.0483	1.0450	1.0435	1.0456
C.30.40.1	30	40	1	1.0886	1.0871	1.0839	1.0865
C.30.40.2	30	40	2	1.0982	1.0940	1.0913	1.0945
C.30.40.4	30	40	4	1.0634	1.0615	1.0605	1.0618
C.60.40.1	60	40	1	1.0189	1.0165	1.0179	1.0178
C.60.40.2	60	40	2	1.0319	1.0311	1.0296	1.0309
C.60.40.4	60	40	4	1.0329	1.0317	1.0316	1.0321
C.10.50.1	10	50	1	1.0599	1.0541	1.0556	1.0565
C.10.50.2	10	50	2	1.0337	1.0325	1.0317	1.0326
C.10.50.4	10	50	4	1.0600	1.0600	1.0583	1.0594
C.30.50.1	30	50	1	1.0703	1.0649	1.0676	1.0676
C.30.50.2	30	50	2	1.0443	1.0428	1.0394	1.0422
C.30.50.4	30	50	4	1.0793	1.0746	1.0728	1.0756
C.60.50.1	60	50	1	1.0561	1.0522	1.0545	1.0543
C.60.50.2	60	50	2	1.0838	1.0814	1.0823	1.0825
C.60.50.4	60	50	4	1.0233	1.0193	1.0183	1.0203

ANNEXE 2: CONDITIONS OF DYEING OF COTTON FIBRE

Samples	Mass (g)	Ratio of oxidation [30:1] NaIO4 (2 g/L) (ml)	Ratio of Lupasol® P [20:1] (ml)	Ratio of reactive dye [20:1] (ml)	Alkali (20 g/L) Sodium Carbonate, Na2CO3 (g)	Alkali(3 mL/L) Sodium Hydroxide NaOH 36° Be (mL)	Salt (70 g/L) Sodium sulphate, NaSO4 (g)	3.5% owf Reactive dye (g)
ORI0	4.568	-	-	91.352	1.827	0.274	-	0.160
ORI5	4.588	-	-	91.760	1.835	0.275	3.212	0.161
ORI1	4.518	-	-	90.352	1.807	0.271	6.325	0.158
OXP0	4.515	135.447	90.298	90.298	1.806	0.271	-	0.158
OXP5	4.536	136.083	90.722	90.722	1.814	0.272	3.175	0.159
Total	**26.750**	**271.530**	**181.020**	**535.004**	**10.700**	**1.605**	**12.712**	**0.936**

ANNEXE 3: ALDEHYDE CONTENT OF OXIDIZEDCOTTON FIBRE

	Sample	Mass of sample, m (g)	pH before	pH after	Volume of NaOH consumed by the sample, V_2 (mL)	Average volume of NaOH, V_2 (mL)
Concentration of NaOH 0.1 M	Original 1	0.1057	3.94	4.02	0.10	0.10
	Original 2	0.1022	3.93	4.04	0.10	
Concentration of NaOH 0.01 M	Original 3	0.1050	3.95	4.00	0.85	0.65
	Original 4	0.1047	3.93	4.01	0.45	

Sample	Mass of the sample, m (g)	pH before	pH after	Volume of NaOH consumed by the sample, V_1 (mL)	Aldehyde content (%)
A.10.30.1	0.1011	3.88	4.06	0.20	1.602
A.10.30.2	0.1006	3.88	4.03	0.20	1.610
A.10.30.4	0.1069	3.84	4.03	0.20	1.515
A.30.30.1	0.1086	3.86	4.01	0.20	1.492
A.30.30.2	0.1026	3.88	4.00	0.20	1.579
A.30.30.4	0.0988	3.88	4.04	0.20	1.640
A.60.30.1	0.1032	3.47	4.07	0.40	4.709
A.60.30.2	0.1048	3.80	4.06	0.25	2.319
A.60.30.4	0.0970	3.85	4.00	0.20	1.670
A.10.40.1	0.1081	3.90	4.00	0.15	0.749
A.10.40.2	0.1057	3.90	4.03	0.10	0.000
A.10.40.4	0.1000	3.87	4.01	0.20	1.620
A.30.40.1	0.1063	3.88	4.06	0.20	1.524
A.30.40.2	0.1092	3.88	4.03	0.15	0.742
A.30.40.4	0.1043	3.83	4.03	0.20	1.553
A.60.40.1	0.9980	3.89	4.02	0.15	0.081
A.60.40.2	0.1019	3.87	4.03	0.20	1.590
A.60.40.4	0.1034	3.83	4.00	0.20	1.567
A.10.50.1	0.1061	3.85	4.03	0.20	1.527
A.10.50.2	0.1040	3.88	4.00	0.15	0.779
A.10.50.4	0.1039	3.82	4.03	0.25	2.339
A.30.50.1	0.1055	3.88	4.00	0.15	0.768
A.30.50.2	0.1059	3.82	4.00	0.20	1.530
A.30.50.4	0.1062	3.79	4.02	0.25	2.288
A.60.50.1	0.1070	3.88	4.01	0.25	2.271
A.60.50.2	0.1033	3.81	4.02	0.20	1.568
A.60.50.4	0.1060	3.74	4.03	0.30	3.057

Sample	Mass of the sample, m (g)	pH before	pH after	Volume of NaOH consumed by the sample, V_1 (mL)	Aldehyde content (%)
B.10.30.1	0.1057	3.92	4.03	1.00	0.536
B.10.30.2	0.1073	3.92	4.04	1.20	0.830
B.10.30.4	0.1048	3.88	4.01	1.40	1.159
B.30.30.1	0.1074	3.87	4.00	1.20	0.830
B.30.30.2	0.1064	3.85	4.01	1.20	0.837
B.30.30.4	0.0993	3.84	4.01	1.95	2.121
B.60.30.1	0.1058	3.93	4.02	1.10	0.689
B.60.30.2	0.1040	3.89	4.02	1.20	0.857
B.60.30.4	0.1075	3.87	4.00	1.20	0.829
B.10.40.1	0.1056	3.93	4.02	1.00	0.537
B.10.40.2	0.1040	3.92	4.00	1.00	0.545
B.10.40.4	0.1046	3.89	4.02	1.30	1.007
B.30.40.1	0.1004	3.93	4.02	1.05	0.645
B.30.40.2	0.1056	3.90	4.00	1.15	0.767
B.30.40.4	0.1033	3.88	4.00	1.40	1.176
B.60.40.1	0.1036	3.90	4.00	1.00	0.547
B.60.40.2	0.1052	3.89	4.01	1.20	0.847
B.60.40.4	0.1044	3.85	4.00	1.50	1.319
B.10.50.1	0.1082	3.88	4.00	1.35	1.048
B.10.50.2	0.1053	3.87	4.01	1.30	1.000
B.10.50.4	0.1053	3.81	4.00	1.65	1.538
B.30.50.1	0.1048	3.84	4.01	1.20	0.850
B.30.50.2	0.1073	3.81	4.00	1.55	1.359
B.30.50.4	0.1052	3.82	4.00	1.95	2.002
B.60.50.1	0.1062	3.85	4.06	1.30	0.992
B.60.50.2	0.1049	3.80	4.00	1.80	1.776
B.60.50.4	0.1086	3.70	4.00	2.40	2.610

Sample	Mass of the sample, m (g)	pH before	pH after	Volume of NaOH consumed by the sample, V_1 (mL)	Aldehyde content (%)
C.10.30.1	0.1090	3.87	4.01	0.95	0.446
C.10.30.2	0.1078	3.87	4.03	1.10	0.676
C.10.30.4	0.1070	3.86	4.00	1.20	0.833
C.30.30.1	0.1070	3.87	4.00	1.00	0.530
C.30.30.2	0.1028	3.86	4.03	1.05	0.630
C.30.30.4	0.1068	3.84	4.00	1.20	0.834
C.60.30.1	0.1081	3.88	4.01	0.90	0.375
C.60.30.2	0.1018	3.87	4.01	1.10	0.716
C.60.30.4	0.1061	3.80	4.00	1.25	0.916
C.10.40.1	0.1029	3.85	4.00	1.35	1.102
C.10.40.2	0.1042	3.84	4.00	1.55	1.399
C.10.40.4	0.1068	3.81	4.01	1.80	1.744
C.30.40.1	0.1057	3.85	4.01	1.30	0.996
C.30.40.2	0.1071	3.78	4.00	1.70	1.588
C.30.40.4	0.1045	3.76	4.00	2.00	2.093
C.60.40.1	0.1017	3.81	4.00	1.40	1.195
C.60.40.2	0.1056	3.80	4.00	1.80	1.764
C.60.40.4	0.1028	3.76	4.06	2.00	2.127
C.10.50.1	0.1064	3.86	4.01	1.15	0.761
C.10.50.2	0.1080	3.85	4.01	1.45	1.200
C.10.50.4	0.1067	3.82	4.03	1.80	1.746
C.30.50.1	0.1067	3.85	4.01	1.50	1.291
C.30.50.2	0.1061	3.85	4.01	1.60	1.451
C.30.50.4	0.1051	3.81	4.00	1.80	1.773
C.60.50.1	0.1043	3.74	4.01	2.00	2.097
C.60.50.2	0.1050	3.76	4.01	2.60	3.009
C.60.50.4	0.1084	3.72	4.02	2.50	2.765

ANNEXE 4: TENSILE STRENGTH OF OXIDIZED COTTON FIBRE

Sample	Maximum force, Rm (N)	Elongation at max break, ε (%)	Breaking force, RB (N)	Elongation at break, ε (%)
1	187.57	168.64	119.52	169.87
2	174.35	168.26	49.88	172.33
3	187.68	171.25	89.47	174.39
4	178.35	160.92	151.44	162.44
5	173.93	167.5	150.6	169.35
Average	180.376	167.314	112.182	169.676

Time t (min)	Temperature, T (ºC)	Concentration of periodate NaIO4 (g/L)	Maximum force, Rm (N)			Average maximum force, (N)	Elongation at maximum force ε (%)			Average elongation at max force, ε (%)
			Sample A	Sample B	Sample C		Sample A	Sample B	Sample C	
10	30	1	153.43	172.20	155.42	154.43	150.34	150.37	140.80	147.17
10	30	2	147.88	129.35	148.94	148.41	151.90	144.29	146.15	147.45
10	30	4	130.23	150.28	140.31	140.27	140.44	141.80	135.39	139.21
30	30	1	155.61	145.80	167.88	156.43	162.36	142.76	157.12	154.08
30	30	2	120.02	133.54	141.79	131.78	120.43	148.68	134.66	134.59
30	30	4	120.63	128.22	108.09	124.43	136.82	144.99	136.99	139.60
60	30	1	109.06	136.11	142.82	139.47	138.65	144.72	155.56	146.31
60	30	2	108.22	155.33	129.35	130.97	125.70	147.39	145.68	139.59
60	30	4	78.17	104.22	114.75	109.49	122.25	121.29	144.49	129.34
10	40	1	161.00	165.65	149.26	163.33	163.06	147.41	132.00	147.49
10	40	2	131.12	147.34	149.66	142.71	129.95	147.04	144.09	140.36
10	40	4	120.16	126.38	143.78	123.27	139.05	141.44	143.78	141.42
30	40	1	109.10	146.00	160.28	153.14	144.24	155.75	145.60	148.53
30	40	2	119.25	123.42	158.54	121.34	132.49	132.54	146.66	137.23
30	40	4	114.13	123.10	120.08	119.10	131.29	134.27	135.49	133.68
60	40	1	137.58	142.53	134.77	138.29	127.89	140.63	112.97	127.16
60	40	2	126.20	107.52	124.97	125.59	148.65	125.55	128.96	134.39
60	40	4	137.58	96.34	110.50	103.42	127.89	125.70	113.80	122.46
10	50	1	162.14	147.39	123.28	144.27	152.96	151.97	114.99	139.97
10	50	2	142.92	133.84	134.09	136.95	110.29	128.39	138.90	125.86
10	50	4	162.14	111.59	116.67	114.13	152.96	135.52	121.70	136.73
30	50	1	145.24	118.87	132.09	132.07	147.25	142.99	136.09	142.11
30	50	2	151.00	102.20	113.30	107.75	2258.57	127.63	131.96	129.80
30	50	4	86.81	87.12	99.27	91.07	128.75	130.85	127.11	128.90
60	50	1	141.01	111.50	128.93	120.22	147.26	131.62	131.77	136.88
60	50	2	110.76	83.55	97.09	97.13	142.28	129.00	124.53	131.94
60	50	4	94.80	65.39	90.88	92.84	128.12	121.06	118.48	122.55

Time t (min)	Temperature, T (ºC)	Concentration of periodate NaIO4 (g/L)	Breaking force, RB (N)			Average breaking force, (N)	Elongation at break, ε_{break} (%)			Average elongation at break, ε (%)
			Sample A	Sample B	Sample C		Sample A	Sample B	Sample C	
10	30	1	75.83	130.38	95.06	100.42	154.15	152.73	143.73	150.20
10	30	2	77.17	57.29	49.60	61.35	156.19	151.13	157.26	154.86
10	30	4	79.85	103.54	56.13	79.84	146.49	145.52	139.64	143.88
30	30	1	87.86	65.40	85.62	79.63	165.29	146.67	160.34	157.43
30	30	2	51.20	124.10	71.98	82.43	127.98	150.86	139.57	139.47
30	30	4	77.96	124.31	53.65	85.31	139.89	145.39	144.77	143.35
60	30	1	42.03	52.08	57.97	50.69	147.65	151.09	159.92	152.89
60	30	2	43.81	119.37	115.58	92.92	133.00	149.49	149.15	143.88
60	30	4	30.02	37.37	83.90	50.43	130.84	129.53	146.18	135.52
10	40	1	45.08	63.50	76.07	61.55	165.77	150.87	135.96	150.87
10	40	2	87.58	43.57	48.67	59.94	134.42	152.37	150.82	145.87
10	40	4	34.44	95.45	87.53	72.47	143.73	145.33	141.72	143.59
30	40	1	34.18	72.43	46.87	51.16	152.67	160.87	151.79	155.11
30	40	2	44.12	57.63	49.62	50.46	137.17	140.29	149.84	142.43
30	40	4	87.15	88.22	52.63	76.00	134.23	136.00	140.55	136.93
60	40	1	70.53	99.56	65.77	78.62	131.44	143.54	117.85	130.94
60	40	2	42.46	53.63	42.34	46.14	155.64	130.44	132.74	139.61
60	40	4	70.53	23.77	42.59	45.63	131.44	131.19	119.88	127.50
10	50	1	52.04	71.82	43.21	55.69	157.55	155.33	120.96	144.61
10	50	2	72.42	44.48	99.00	71.97	116.95	133.04	142.16	130.72
10	50	4	52.04	49.67	88.40	63.37	157.55	141.37	123.01	140.64
30	50	1	110.69	36.46	116.46	87.87	149.78	150.08	138.90	146.25
30	50	2	64.75	26.15	42.84	44.58	2285.82	132.47	139.92	136.20
30	50	4	58.68	42.53	92.24	64.48	132.67	135.65	127.65	131.99
60	50	1	42.49	46.65	68.45	52.53	153.14	136.28	135.99	141.80
60	50	2	46.99	28.04	30.86	35.30	146.48	135.52	129.83	137.28
60	50	4	81.78	44.64	81.12	69.18	130.79	124.69	118.99	124.82

Time, t (min)	Temperature, T (°C)	Concentration of periodate, [NaIO4] (g/L)	Average aldehyde content, AC (%)	Average maximum force, Fmax (N)	Strength Loss	Fmax * AC
Untreated				180.376		
10	30	1	0.491	154.43	14.39	75.845
30	30	1	0.753	156.43	13.28	117.841
60	30	1	0.996	139.47	22.68	138.911
10	30	2	0.680	148.41	17.72	100.883
30	30	2	0.734	131.78	26.94	96.713
60	30	2	1.478	130.97	27.39	193.511
10	30	4	0.532	140.27	22.23	74.604
30	30	4	0.786	124.43	31.02	97.850
60	30	4	0.872	109.49	39.30	95.523
10	40	1	0.819	163.33	9.45	133.843
30	40	1	0.972	153.14	15.10	148.885
60	40	1	1.376	138.29	23.33	190.228
10	40	2	0.821	142.71	20.88	117.136
30	40	2	1.178	121.34	32.73	142.889
60	40	2	1.635	125.59	30.38	205.269
10	40	4	0.871	123.27	31.66	107.367
30	40	4	1.306	119.10	33.97	155.499
60	40	4	1.723	103.42	42.66	178.213
10	50	1	0.905	144.27	20.02	130.517
30	50	1	1.100	132.07	26.78	145.273
60	50	1	1.411	120.22	33.35	169.680
10	50	2	1.070	136.95	24.08	146.586
30	50	2	1.405	107.75	40.26	151.352
60	50	2	1.887	97.13	46.15	183.315
10	50	4	1.544	114.13	36.73	176.237
30	50	4	2.392	91.07	49.51	217.856
60	50	4	2.688	92.84	48.53	249.519

ANNEXE 5: STRENGTH LOSS AND F_{MAX} X AC

ANNEXE 6: COLOUR MEASUREMENT

Sample	State	L*	a*	b*	C*	h	DL*	Da*	Db*	DC*	DH*	DE*ab	Pasa/No pasa
ORI1	SCE/100	61.1342	45.1105	14.3471	47.337	17.6429							
ORI5	SCE/100	60.7566	43.013	12.924	44.9126	16.7239	-0.3776	-2.0975	-1.4231	-2.4244	-0.7396	2.5627	NO PASA
ORI0	SCE/100	69.5905	28.5623	8.9658	29.9364	17.4273	8.4564	-16.5482	-5.3813	-17.4006	-0.1416	19.3471	NO PASA
OXP0	SCE/100	60.2686	31.0358	16.8	35.2911	28.4272	-0.8655	-14.0747	2.453	-12.046	7.6818	14.3131	NO PASA
OXP5	SCE/100	48.9676	44.0054	24.403	50.3188	29.0104	-12.1666	-1.1051	10.0559	2.9817	9.6671	15.823	NO PASA

Sample	400	410	420	430	440	450	460	470	480	490	500	510	520	530	540	550	560	570	580	590	600	610	620	630	640	650	660	670	680	690	700
ORI1	19.76	20.78	21.72	22.45	22.86	22.54	21.2	19.27	17.21	15.58	14.28	13.51	13.43	13.76	14.36	15.81	19.44	26.4	36.86	49.16	60.43	68.74	74.09	77.35	79.47	81.11	82.45	83.59	84.56	85.5	86.34
ORI5	20.13	21.15	22.09	22.82	23.23	22.94	21.63	19.75	17.67	16.03	14.72	13.94	13.82	14.13	14.73	16.17	19.7	26.44	36.37	47.86	58.3	65.89	70.62	73.32	74.92	76.06	76.99	77.77	78.57	79.42	80.3
ORI0	30.38	31.41	32.47	33.42	34.19	34.56	34.23	33.21	31.67	30.22	28.82	27.78	27.46	27.69	28.36	29.81	33.11	39.11	47.39	56.33	63.9	69.14	72.37	74.27	75.42	76.29	76.99	77.55	78.13	78.83	79.58
OXP0	16.23	17.15	18.08	18.78	19.36	19.62	19.45	18.88	18.06	17.33	16.76	16.53	16.74	17.28	18.24	20.17	23.72	29.11	35.66	42.3	48.12	52.96	57.04	60.46	63.35	65.91	68.15	70.01	71.69	73.27	74.77
OXP5	8.16	8.57	8.88	9.07	9.17	9.03	8.46	7.69	6.89	6.32	5.96	5.9	6.1	6.43	6.97	8.21	10.99	16.08	23.42	31.73	39.22	45.17	49.8	53.4	56.31	58.89	61.32	63.65	65.91	68.08	70.18

Sample	400	410	420	430	440	450	460	470	480	490	500	510	520	530	540	550	560	570	580	590	600	610	620	630	640	650	660	670	680	690	700
ORI1	1.6292	1.5101	1.4106	1.3394	1.3015	1.331	1.4645	1.6911	1.9913	2.2871	2.5728	2.7685	2.7902	2.7025	2.5537	2.2416	1.6692	1.0259	0.5408	0.2629	0.1296	0.0711	0.0453	0.0332	0.0265	0.022	0.0187	0.0161	0.0141	0.0123	0.0108
ORI5	1.5845	1.4698	1.3739	1.3052	1.2685	1.2943	1.4198	1.6304	1.918	2.1993	2.4703	2.6565	2.687	2.6092	2.4681	2.173	1.6366	1.0233	0.5566	0.284	0.1491	0.0883	0.0611	0.0485	0.042	0.0377	0.0344	0.0318	0.0292	0.0267	0.0242
ORI0	0.7977	0.7489	0.7022	0.6632	0.6334	0.6196	0.6319	0.6716	0.7371	0.8056	0.879	0.9388	0.9581	0.9442	0.9048	0.8263	0.6757	0.474	0.292	0.1693	0.102	0.0689	0.0527	0.0446	0.0401	0.0368	0.0344	0.0325	0.0306	0.0284	0.0262
OXP0	2.1619	2.0012	1.8559	1.7563	1.6794	1.6465	1.6679	1.7427	1.8588	1.9718	2.0671	2.1075	2.0706	1.9799	1.8324	1.5798	1.2265	0.8632	0.5804	0.3935	0.2797	0.2089	0.1618	0.1293	0.106	0.0882	0.0744	0.0642	0.0559	0.0488	0.0426
OXP5	5.1683	4.8772	4.675	4.558	4.4984	4.5822	4.9525	5.5404	6.2913	6.943	7.4191	7.5041	7.2272	6.8082	6.2085	5.1312	3.6045	2.1899	1.252	0.7344	0.471	0.3328	0.253	0.2033	0.1695	0.1435	0.122	0.1038	0.0882	0.0748	0.0634